THE UNIVERSITY OF MICHIGAN

INDUSTRY PROGRAM OF THE COLLEGE OF ENGINEERING

ADSORPTION OF NITROGEN-METHANE ON LINDE MOLECULAR SIEVE TYPE 5A

Peter B. Lederman

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy in The
University of Michigan
1961

March, 1961

IP-502

Doctoral Committee:

Professor Brymer Williams, Chairman
Associate Professor Lee O. Case
Professor Donald L. Katz
Professor Guiseppe Parravano
Associate Professor M. Rasin Tek

ACKNOWLEDGEMENT

The author wishes to take this opportunity to thank the many people who have assisted in the completion of this thesis.

Among these are Dr. T. L. Thomas of the Linde Company, who kindly supplied the Molecular Sieve and whose advice was most helpful; Mr. R. L. Porter of Autoclave Engineers for his as well as his associates' valuable time in aiding to solve some valve problems; Mr. Foglesong of The Babcock and Wilcox Company for his help in obtaining material for the adsorption vessel; The Kolene Corporation for Tufftriding some vital parts and the Dow Chemical Company for its gift of the necessary Styrofoam insulation.

Special thanks are due to Messers. Cleatis Bolen, John Wurster, William Hines, and Peter Severn, who assisted in building the equipment and were always ready with helpful suggestions. Mr. Frank Drogoz also deserves many thanks as do his assistants, Richard Naragon and David Williams for the help in the mass spectrometer analysis. Mr. Jude Sommerfeld assisted with the surface area determinations. The staff of the University Computing Center and the use of the IBM 704 Computer materially lightened the task of reducing the experimental data to a useful form.

To his committee the author desires to extend a special note of thanks for their patience, ever open doors and encouragement.

The Industry Program of the College of Engineering was of great assistance in preparing the final manuscript and in arranging for its presentation in this form.

The encouragement given me by my wife, as well as her aid in preparing the final draft was most helpful.

Finally, to my parents, for making this task possible, and for their continuing encouragement and guidance, I dedicate this work.

TABLE OF CONTENTS

Page

ACKNOWLEDGMENT.. ii

LIST OF TABLES.. vi

LIST OF FIGURES... viii

LIST OF APPENDICES.. x

NOMENCLATURE.. xi

ABSTRACT.. xiii

INTRODUCTION.. 1

DISCUSSION OF THEORY.. 2

- Pure Component Adsorption Isotherms.................... 2
- Adsorption from Mixtures............................... 11

EQUIPMENT... 15

- Adsorption Apparatuses................................. 15
- The Present Apparatus.................................. 17
- The Adsorption Cell.................................... 22
- The Pressure Transducer................................ 24
- Material Selection..................................... 28
- Valve Operation at Low Temperature..................... 28
- Temperature Measurement and Control.................... 30
- Safety Considerations.................................. 31
- Leakage in the System.................................. 32
- Calibration of Equipment............................... 34

EXPERIMENTAL METHOD... 37

- Adsorbent.. 37
- Gases.. 38
- Experimental Method.................................... 40
- Sampling... 42
- Method of Calculating Adsorption Equilibrium........... 44
- Errors in Measurement.................................. 47

EXPERIMENTAL RESULTS.. 52

- Pure Component Adsorption.............................. 52
- Binary Adsorption...................................... 57

TABLE OF CONTENTS CONT'D

Page

DISCUSSION OF RESULTS.. 63

Pure Component Adsorption Calculations.................. 63
Correlations for Total Adsorption from a Mixture........ 70
Adsorption of Components from a Mixture................. 72
Computing Adsorption Loading from the Correlations...... 75
An Adsorption Model..................................... 80

CONCLUSIONS AND RECOMMENDATIONS.............................. 81

BIBLIOGRAPHY... 130

LIST OF TABLES

Table		Page
I	Norwood Pressure Transducer Specifications........	26
II	Calibrated Volumes...............................	35
III	Analyses of Pure Feed Gases......................	39
IV	Paired Samples from Adsorption Cell..............	43
V	Replicate Analyses of a Single Sample............	43
VI	Replicate Samples from a Uniform Mixture.........	43
VII	Accuracy of Measuring Devices....................	49
VIII	Maximum Error Propagated in Pure Component Equilibrium Data................................	50
IX	Maximum Error Propagated in Binary Equilibrium Data..	50
X	Pure Methane Adsorption..........................	54
XI	Pure Nitrogen Adsorption.........................	56
XII	Mixed Adsorption at 295°K Average Temperature.....	58
XIII	Mixed Adsorption at 195°K Average Temperature.....	59
XIV	Mixed Adsorption at 175°K Average Temperature.....	60
XV	Mixed Adsorption at 123°K Average Temperature.....	60
XVI	Confidence Limits on Equilibrium Values...........	61
XVII	Actual and Predicted Binary Adsorption...........	79
XVIII	Explanation of Experimental Data.................	86
XIX	Experimental Data................................	87
XX	Thermocouple Calibration Data....................	99
XXI	Calibration Data for Pressure Gauges.............	100
XXII	Calibration Data for 2000 Psi Pressure Transducer.	104
XXIII	Calibration Data for 2000 Psi Pressure Transducer.	105

LIST OF TABLES CONT'D

Table		Page
XXIV	Calibration Data for 500 Psi Pressure Transducer..	108
XXV	Calculation of "BET" Surface Area Determination 1.	112
XXVI	Calculation of "BET" Surface Area Determination 2.	114
XXVII	Sample Print Out From Computer Calculation........	127
XXVIII	Adsorption of Helium.............................	128

LIST OF FIGURES

Figure		Page
1	Flow Diagram of Adsorption Apparatus.............	18
2	Top View of Closed Bath..........................	19
3	Open Constant Temperature Bath...................	20
4	Instrument and Control Section...................	21
5	Adsorption Cell in Cross Section.................	23
6	Schematic Diagram of Norwood Pressure Transducer...	25
7	Simplified Schematic of Electrical Measuring Circuit..	27
8	Cross Section of Main Block Valve................	29
9	Methane Adsorption Isotherms on 5A Molecular Sieve..	53
10	Nitrogen Adsorption Isotherms on 5A Molecular Sieve..	55
11	Total Mixed Adsorption as a Function of Pressure and Temperature..................................	62
12	Pure Component Adsorption on 5A Molecular Sieve...	64
13	Constants for the Freundlich Equation for Nitrogen and Methane and their Mixtures..........	65
14	Langmuir Constants for Pure Component Adsorption..	66
15	Volume of Nitrogen Adsorbed as a Function of the Adsorption Driving Force........................	68
16	Volume of Methane Adsorbed as a Function of the Adsorption Driving Force........................	69
17	Volume of Nitrogen-Methane Mixtures Adsorbed as a Function of the Adsorption Driving Force.......	71
18	Langmuir Constants for Adsorption from Nitrogen-Methane Mixtures...............................	74

LIST OF FIGURES CONT'D

Figure Page

19 Total Adsorption Correlation on Molecular Sieve 5A.. 76

20 Relative Volatility as a Function of Pressure..... 77

21 Calibration for 300 Psi Pressure Gauge............ 101

22 Calibration for 800 Psi Pressure Gauge............ 102

23 Calibration for 2000 Psi Pressure Gauge........... 103

24 Calibration for 2000 Psi Pressure Transducer...... 106

25 Calibration for 2000 Psi Pressure Transducer...... 107

26 Calibration for 500 Psi Pressure Transducer....... 109

27 Calibration for 500 Psi Pressure Transducer....... 110

28 "BET" Plot for Surface Area Determination 1....... 113

29 "BET" Plot for Surface Area Determination 2....... 115

30 Computer Flow Diagram for Equilibrium Adsorption Loading Calculation................................. 125

31 Computer Flow Diagram for B-W-R Equation Solution for Density and Fugacity.......................... 126

LIST OF APPENDICES

Appendix		Page
A	Experimental Data..................................	84
B	Calibrations.......................................	98
C	Calculation of Surface Area........................	111
D	Pressure Vessel Design Calculations................	116
E	Sample Calculation of Adsorption Equilibrium......	119
F	Adsorption of Helium...............................	128

NOMENCLATURE

a	constant in single component Langmuir equation; milligram moles/gm. atm.
a'	constant in multicomponent Langmuir equation; milligram moles/gm. atm.
b	constant in single component Langmuir equation; 1/atm.
b'	constant in multicomponent Langmuir equation; 1/atm.
b''	constant in multicomponent Langmuir equation; 1/atm.
b_v	van der Waals' constant; cc./gm. mole
E	Schay's mixing coefficient
f	fugacity
k	constant in Freundlich equation; milligram moles/gm.
N	amount adsorbed; milligram moles/gm.
N'	amount adsorbed as pure component under the same pressure as the component partial pressure in the gas phase mixture.
n	constant in Freundlich equation
P	pressure; atm.
R	universal gas constant
T	temperature °Kelvin
v	volume adsorbed
x	mole fraction adsorbed phase
y	mole fraction gas phase
γ	constant
ϵ	adsorption potential; calories/gm. mole
ρ	density; gm. moles/cc.

Subscripts

cr	critical
F	final
FS	free space (adsorption cell)
I	initial
i	i^{th} component
m	maximum
s	at saturation conditions

ABSTRACT

The adsorption of nitrogen and methane and their mixtures on Linde Type 5A Molecular Sieve has been studied in a batch system from -140°C to room temperature and at pressures up to 85 atmospheres. The amount adsorbed at equilibrium is reported for the pure components. Data indicating the equilibrium gas and adsorbate compositions, as well as the total amount adsorbed, are presented for mixtures of nitrogen and methane.

Constants for the Langmuir equation, over the range of pressure and temperature studied, have been obtained for pure component adsorption. The Freundlich equation constants are also presented for the adsorption of pure nitrogen and methane and for total adsorption of mixtures as a function of temperature. The equations with the appropriate constants represent the capacity of the Molecular Sieve for pure components within five per cent and for mixtures within seven per cent of the total amount adsorbed.

Individual component adsorption from mixtures may be expressed as a function of the pressure of the components in the gas phase in equilibrium with the adsorbate. Constants for the system studied are presented as a function of temperature between 100°Kelvin and 300°Kelvin.

Limited data at room temperature for some other adsorbents, such as silica gel and some activated carbons, indicate that Molecular Sieves have a higher capacity for methane and nitrogen. A study made on another activated charcoal which had a slightly greater capacity shows that available surface area is a critical factor in determining capacity.

INTRODUCTION

The present study was undertaken to analyze the adsorption system nitrogen - methane - Linde Molecular Sieve Type 5A*. A method of predicting the adsorbate loading from both pure and mixed gas streams was to be developed. If possible, a model for the adsorption mechanism was to be postulated.

The nitrogen - methane system is of ever growing interest because these two gases appear together in many industrial applications. In addition, the present program to conserve helium will require removal of nitrogen and methane from that gas in varying quantities, for subsequent recovery.

The study, as undertaken, included a wide range of temperatures from room temperature to below the critical of the two gases as well as the pressure range of industrial interest. Temperatures varied from 123° Kelvin to 295°Kelvin and pressures ranged from essentially one atmosphere to as high as 50 atmospheres. The range of compositions at the higher temperatures varied from pure methane to pure nitrogen, while at the lower temperatures, only one or two mixtures were evaluated in addition to the pure components.

For purpose of completeness, a discussion of the various adsorption theores has been included, followed by a discussion of the experimental equipment. The experimental method and results are described and evaluated together with a series of conclusions and recommendations.

---

* Registered Trade Mark

DISCUSSION OF THEORY

Pure Component Adsorption Isotherms

Several basic approaches to physical adsorption equilibrium have been presented since the phenomenon was first observed by Scheele in 1773.(13) These may roughly be distinguished as the kinetic and the thermodynamic approaches. This distinction is somewhat artifical as the isotherms based on the kinetic approach, first advanced by Langmuir,(33,34) can be readily developed from thermodynamic or statistical principles. In the present context an isotherm defines the amount adsorbed as a function of pressure at constant temperature.

Langmuir first derived the isotherm which bears his name:

$$N = \frac{N_m bP}{1 + bP} \tag{1}$$

or

$$N = \frac{aP}{1 + bP} \tag{1a}$$

from kinetic principles(34). This derivation requires that arbitrary forward and reverse rates be balanced. Fowler and Guggenheim(20) have derived the Langmuir isotherm on statistical grounds, considering that the adsorbed molecules do not interact with each other and had no translational motion and were thus confined to localized sites, or points of active adsorption. If one examines the Langmuir isotherm, one can readily see that at high pressures N approaches N_m which corresponds to the amount of adsorbate in a complete monolayer.

While the Langmuir isotherm fitted a great deal of experimental data, the three basic assumptions:

1. Uniform sites with no interaction between adsorbate molecules,
2. No translational motion on the surface,
3. The maximum adsorption corresponds to a complete monolayer,

placed severe restrictions on the theory. Brunauer, Emmett and Teller(15) in their well-known "B E T" equation made the first significant advance when they considered multilayers. The "B E T" equation takes several forms, of which

$$\frac{N}{N_m} = \frac{c\ P/P_s}{(1-P/P_s)[1 + (c-1)P/P_s]} \qquad (2)$$

where the number of layers, or stacks of molecules above the solid surface are finite, is the most widely used form. Several modifications of the original "B E T" equation were proposed by Brunauer et al.(15), where the number of layers are limited, and Brunauer and Demming(14) for the case of adsorption on capillary walls. Joyner(31) has discussed in detail a method of determining the number of adsorption layers in the complete "B E T" equation by graphical methods.

The original derivation of the "B E T" isotherm suffered from the same limitation that Langmuir's derivation did, in that it was based on kinetic equilibria. Hill(24) and others have derived the equation from statistical principles, based on a model allowing vertical but no horizontal interaction between molecules. The "B E T" equation still suffers from the same basic deficiencies as the Langmuir isotherm: no interaction of adsorbate molecules and no lateral motion of the adsorbate molecules in any given layer. More recently, a multi-molecular adsorption model, allowing for lateral interaction, has been suggested by Lee(35).

Unfortunately, no experimental work has been done to confirm the postulated isotherm.

Peierls(46) and Wang(61) derived the Langmuir equation from statistical principles for adsorbed atoms, exhibiting attractive and repulsive interaction respectively. Schay(56) has derived Langmuir's isotherm on statistical grounds in the case of a mobile monolayer, where the adsorbed molecules exhibit a covolume in the adsorbed state, thus removing the last serious theoretical restriction.

The Freundlich isotherm(21)

$$N = KP^{1/n} \tag{3}$$

has been derived from the Langmuir isotherm by Zeldowitsh(63). By assuming that the adsorption surface is heterogeneous, the Langmuir equation may be written as

$$N = \sum_{i} \frac{a_i P}{P + c_i} \tag{4}$$

where c_i depends mainly on the heat of adsorption on the adsorption spaces and a_i is a function of the number of these spaces. If "c" is said to vary continuously over the surface and the distribution function of "a" assumed the form

$$a(c) = Ac^{1/n-1} \tag{5}$$

then Zeldowitsh arrives at the Freundlich isotherm.

The isotherm may also be derived for multi-molecular adsorption, as was shown by Baly(3), who assumed that each adsorbed layer obeys a Langmuir isotherm with different constants, and that each succeeding layer has a slightly lower heat of adsorption than the one below. These assumptions lead to the Freundlich isotherm for moderate pressures.

More recently, Sips(57,58) has shown that a generalized Freundlich isotherm:

$$N = (P/(P + a))^c \qquad 0 < c < 1 \qquad (6)$$

may be obtained by assuming a localized adsorption model with no interaction. Equation (6) reduces to the Freundlich equation for small "P" , and when "c" is equal to one the Langmuir equation results. Unfortunately, this theory does not appear to fit the experimental data. Sips' assumptions of localized sites and no molecular interaction may be necessary from a mathematical point of view, but present a simplified picture of the physical process, thus leaving much to be desired.

In an excellent review of the integral inversion approach used by Sips, Honig(28) indicates that the isotherm is very insensitive to changes in the chosen distribution function. In addition, all attempts to obtain an isotherm by this method require a model with no molecular interaction. He further states that many of the most useful isotherms do not satisfy all of the mathematical restrictions found to be necessary in applying this method of analysis. The isotherm suggested by Sips is, as he states, the simplest satisfying all the necessary restrictions. A real physical restriction, that at very low pressures, the amount adsorbed is proportional to the pressure is not satisfied except in the case of "c" equal to one. It would seem, then, that Sips' model is too simple to explain the total adsorption isotherm. Real improvements in obtaining valid adsorption isotherms must come from advanced or improved models of the adsorption phenomena.

Redlich and Peterson(52) recently proposed an isotherm

$$N = aP/(1 + cP^{\gamma}) \qquad (7)$$

where $0 < \gamma < 1$

which fits much of the experimental data well. It further reduces to the phenomenalogically sound, limiting Langmuir equation

$$N = ap \qquad (8)$$

at low pressure. At moderate pressure the equation reduces to the Freundlich isotherm

$$N = \frac{a}{c} P^{1-\gamma} \qquad (9)$$

which appears to be sound in this range. The equation, however, breaks down as the pressure becomes very high.

At present the kinetic-statistical approach, while indicating correct avenues, has, due to the limitations imposed by the simplified models, not fully explained the adsorption process.

About the same time that Langmuir first advanced his kinetic adsorption model, Polanyi suggested a model based essentially on thermodynamic principles. As first proposed by Polanyi(47,48,49,50), the theory assumed that long range forces controlled the adsorption. This basic assumption was later modified by Polanyi and Goldman(22), so that the theory would conform with the concept of molecular forces.

Basically, the Potential Theory of Adsorption assumes that work must be done to bring the molecules from the gas phase into the adsorbed phase, and that this work, ϵ, is work of compression:

$$\epsilon = \int_{\rho_g}^{\rho_a} VdP \qquad (10)$$

Then, if any layer "i" is considered, one can obtain the work required, ϵ_i, which is called its potential, and the equipotential surfaces will vary from a maximum of ϵ_o, the potential of the adsorbent-adsorbate interface, to zero, the potential at the gas-adsorbate interface. Each equipotential surface will enclose a given volume, v_i, around the adsorbent. Thus it was shown that the volume adsorbed and the work expended in the adsorption process are related. Polanyi denoted this relationship

$$\epsilon_i = \varphi(v_i) \tag{11}$$

as the characteristic curve dependent only upon the adsorbent-adsorbate system.

Although Polanyi first applied the theory, Berényi(7,8) improved the method considerably. Both found that the computation of the characteristic curve, although fundamentally the same over the whole range of interest, required slight alterations near the critical point and above the critical temperature.

Well below the critical temperature, the characteristic curve may be computed, if one assumes an ideal gas model; 1) by integrating the compressive work integral between the limits of the system and saturation pressures respectively; thus:

$$\epsilon_i = \int_P^{P_s} V dP \tag{10}$$

or

$$\epsilon_i = RT \ln(P_s/P) \tag{10a}$$

and 2) if one assumes an incompressible liquid, the adsorbed volume becomes:

$$v_i = N_i/\rho_s \qquad (12)$$

where ρ_s is taken as the density of the saturated liquid at the adsorption temperature. Berenyi suggested corrective terms for both the potential integral and the density near or above the critical temperature, so that near the critical:

$$\epsilon = RT \ln (P_s/P) + \mu \qquad (13)$$

$$v = N/\rho_s \qquad (12)$$

and above the critical,

$$\epsilon = RT \ln \frac{0.14T}{Pb_v} \qquad (14)$$

where b_v is van der Waals' constant.

The model as originally suggested has been used effectively; more recently modifications have been introduced, in particular for the conditions near or above the critical to remove the trial and error part of the solution for the correction terms originally introduced by Berényi. Nikolaev and Dubinin(43) have proposed that above the critical the potential be computed by:

$$\epsilon = RT \ln \tau^2(P_{cr}/P) \qquad (15)$$

where

$$\tau = T/T_{cr} \qquad (16)$$

and the adsorbate volume:

$$v = Nb_v \quad .$$

They obtain this result by showing at the critical temperature the characteristic curve obtained using the normal method of evaluating ϵ;

$$\epsilon = RT_{cr} \ln (P_{cr}/P) \qquad (17)$$

and using Berenyi's modification above the critical

$$\epsilon = RT_{cr} \ln \mu \ (P_{cr}/P) \qquad (18)$$

will coincide when

$$\mu = (P_{cr}b_V/T_{cr}) \ \tau \qquad (18a)$$

In addition, Nikolaev and Dubinin(43,17) suggests that above the normal boiling point a density:

$$\rho^* = \rho_s - ((\rho_s - \rho_V)/(t_{cr} - t_s))(t - t_s) \qquad (19)$$

where ρ_V is equal to van der Waals' constant, would better represent the density of the adsorbate. This density then will take into account the existence of the adsorbate in a compressed state due to the attractive forces of the adsorbent.

The deviation from ideality of the gas in equilibrium with the adsorbate should influence the adsorption potential. Although Polanyi in his original work suggests this, he did not develop the idea. Lewis and co-workers(27), in correlating some adsorption isotherms of hydrocarbons at moderate pressures, found that the deviations were sufficient to warrant introducing corrections for the deviations from ideality. They suggest the use of fugacity, the most reasonable approach, instead of pressure. Thus,

$$\epsilon = RT \ln (f_s/f) \qquad (20)$$

where, from their calculations, f_s is the fugacity at the saturation pressure, obtained by using the generalized f/p plots. Above the critical

f_s was set equal to the fugacity at the pseudo-saturation pressure as determined by extrapolating the usual vapor pressure curve:

$$\ln P_s = (-A/T) + B \qquad (21)$$

where "A" and "B" are constants.
Lewis and his co-workers suggested that the density of the adsorbate was equal to the saturated liquid density at the adsorption pressure. It would seem that their analysis is quite satisfactory except for their assumption regarding density, as liquid density is principally a function of the system temperature.

A combination of the work of Dubinin and co-workers with that of Lewis should give a better representation of the adsorption potential. Thus, the use of fugacities, to represent the driving force, evaluated at the system pressure and saturation or the critical condition, together with the density evaluated by Dubinin's method should give a good characteristic curve; that is a single function

$$\epsilon = \varphi(v) \qquad (22)$$

independent of temperature.

Although the Potential Theory does not clearly explain the adsorption phenomena, it does present a satisfactory explanation for the gross process. The process above the usual critical point is identical in nature to that below the critical point in that a dense phase forms. This phase, while not a liquid as normally envisioned, does possess many of the same properties. The theory does have the very fine property of generalizing the system from one isotherm. Lack of knowledge regarding the dense or adsorbed phase limits the general applicability of the theory at present. Hopefully, added knowledge in this area will make this theory more useful.

The deterministic approach, illustrated by Hill, Schay and many others may lead to a number of models and isotherm equations. At present, no totally satisfactory model has been suggested to explain in particular the adsorption phenomena at moderate pressures. Most probably, this is the result of the many simplifications necessary to enable one to treat the phenomena from the statistical viewpoint and still obtain mathematical models which may be solved analytically. It may be that by the application of numerical methods at some future date more complex models, which allow for all types of molecular interactions, may be proposed and a more definitive test for determining the applicability of specific models at moderate pressures may be found.

Adsorption From Mixtures

Much of the work done to date on adsorption from gaseous mixtures falls into the category of dehumidification. Some work has been done on removal of trace impurities from gaseous streams. In this area two works, that of Johnson(29) and Hiza(28) are of some interest as they deal with the removal of trace amounts of nitrogen and methane by silicon gel adsorption from a high purity hydrogen stream.

A good review of the early work in mixed adsorption is given by Brunauer.(13) Very little work has been done in this area. The first work of any significance is that of Markham and Benton(40), which extend Langmuir's isotherm to mixtures. Assuming the same model as Langmuir, the component isotherms resulting from the solution of the rate equations (two adsorption and two desorption) are:

$$N_1 = \frac{N_{1m}\, b_1P_1}{1 + b_2P_2 + b_1P_1} \qquad (23a)$$

$$N_2 = \frac{N_{2m}\, b_2P_2}{1 + b_2P_2 + b_1P_1} \qquad (23b)$$

Equations (23a) and (23b) indicate a mutual decrease in the adsorption of both components at a given partial pressure. This has been shown to be true in general; the equation does not take into account the possibility of interaction between the two components in the adsorbed state.

The relationship appears to hold well at low concentrations, but breaks down at the higher concentrations reinforcing the problems caused by interaction. Schay _et al._(57) have developed essentially the same equation as Markham and Benton:

$$N_1 = N_{1m} \frac{a_1P_1/E_1}{1 + \sum_j (a_jP_j/E_j)} \qquad (24)$$

where E_j is a function of the interaction of the molecular species in the adsorbed state and is defined by Schay as:

$$\ln E_k = [\sum_j n_j\beta_j - \beta_k \Sigma n_j / \Sigma n_j\beta_j][\frac{A}{\Sigma n_j\beta_j} \ln(1 - \frac{\Sigma n_j\beta_j}{A}) + 1]$$

β = two dimensional residual molecular volume

A = adsorbent area

n = number of molecules adsorbed at the asymptotic value of the isotherm.

For a binary component, if $E_1 = E_2 = 1$, the result is identical to that of Markham and Benton. In addition, Schay and co-workers have shown that the empirical relationship, for a binary mixture, suggested by Williams(62) and observed by Lewis and Gilliland(36)

$$\frac{N_1}{N'_1} + \frac{N_2}{N'_2} = 1 \tag{25}$$

can be shown to be:

$$\frac{N_1}{N'_1} + \frac{N_2}{N'_2} = 1 + \frac{\frac{1}{P}\left(\frac{P_1}{E_1} + \frac{P - P_1}{E_2}\right) - 1}{1 + \frac{a_1}{E_1} P_1 + \frac{a_2}{E_2}(P - P_1)} \tag{26}$$

for their model. Thus Equation (25) is strictly correct for

$$E_1 = E_2 = 1$$

which indicates essentially no interaction of the species in the adsorbed state. In practice, Schay has found that E_1 and E_2 each differ slightly from unity, one being greater the other less and Lewis' observation is still valid in practice.

Redlich and Peterson(52) have suggested that their equation for pure components (Equation 8) is also valid for mixtures if it is modified in a manner analogous to the Markham modification of Langmuir's isotherm for multi-component adsorption. This results in:

$$N_1 = \frac{a_1 P_1}{1 + c_1 P_1^{\gamma_1} + c_2 P_2^{\gamma_2}} \tag{27}$$

which does not account for any interactions if a_i and c_i are identical values for the mixed isotherm as for the pure component. A modification for interaction of the molecular species, similar to that suggested by Schay, can be introduced so that the form of the equation would be:

$$N_i = \frac{a_i P_i / E_i}{1 + \sum_j (c_j P_j^{1/j} / E_j)} \qquad (28)$$

Very little work has been carried out in the area of co-adsorption of mixtures so that the phenomena of competing adsorption has not been studied except as an extension of pure component adsorption. At the present time it would appear that very little can or should be said in this area until the phenomenon of pure component physical adsorption has been more clearly defined.

A detailed sub-microscopic study of the solid adsorbent surface and the surface forces must be undertaken before a clear picture of the adsorption phenomena can be developed. In addition the molecular state of the adsorbate, both for pure and multicomponent systems, requires examination. Until the adsorption phenomena is clearly established, a semi-empirical approach such as that discussed above, must suffice for engineering purposes.

EQUIPMENT

Adsorption Apparatuses

There are basically three methods of measuring adsorption equilibria, the continuous once-through flow system, the recirculating flow system and the closed system. Each system or method has inherent advantages and disadvantages.

The continuous flow system requires careful control of the flow rates and continuous stream analysis. Both of the requirements can easily present experimental difficulties as they must often be determined and controlled within very small tolerance limits. A modification, used by Linde(51), eliminates these difficulties to some extent. In this modified flow system, adsorbate is passed over the adsorbent bed until flow rates at the entrance and exit of the cell are equal. The cell effluent is then sampled and the cell taken off the line. The adsorbate is desorbed; the desorbed material is collected and its mass and composition determined. Knowing the gas phase composition and volume, the adsorbate volume and composition may be determined by material balance. Both the once-through and modified once-through flow systems require large amounts of adsorbate gas and a great deal of coolant at low temperature. They do, however, enable the experimenter to obtain kinetic data, as well as equilibrium data.

The recirculating flow system, such as the one described by Lewis and co-workers(37), is quite satisfactory for equilibrium data but can present problems as there is a greater possibility of leaks. As it recirculates the gas, a uniform system will be achieved and by appropriate pressure measurements and knowing the free space volume one can determine the amount adsorbed. As it has the additional feature of a large gas space not in contact with the adsorbent, it is easier to control the gas phase equilibrium composition and even the pressure by adding small increments of gas as the adsorption process proceeds. This system requires mechanical agitation, or rocking, which can present problems when considered in respect to a system that must be maintained at low temperatures and high pressures. In addition, the entire system must be leak-free which in itself can be a difficult problem under severe operating requirements and constant movement. This system is probably best adapted to operating pressures below ten atmospheres and temperatures in the ambient region.

By far, in many respects, the simplest system is the closed system in which a measured amount of sample is admitted to the equilibrium vessel and in the case of the mixture, the gas phase is sampled when equilibrium is reached. Then, knowing the amount of each constituent in the gas phase, the equilibrium adsorbate can be determined by material balance. Several variations of this type of apparatus have been used. At low pressures and particularly for pure components, a gravimetric adsorption apparatus, as typified by the sorption balance of McBain and Bakr(38), is very useful in that the amount adsorbed can be determined directly. Sawyer, Josefowitz and Othmer(29) have made modifications to the spring and general assembly which make the apparatus more durable. At high pressure, modifications of this balance have been developed by McBain and Britton(39) and Morris and Mass(42).

Volumetric apparatuses for low pressure work are used frequently. The simplest apparatus of this type is probably that of Pease(44) and is similar to ones used by Homfray, Titoff and others. Coolidge(16) developed an apparatus of this type which had no stopworks. A high pressure volumetric adsorption apparatus which was suitable for work over a wide temperature range was built by Antropff and co-workers.(1) This apparatus is excellent for pure component adsorption studies at high pressure and was used to determine the adsorption isotherms of Nitrogen and Argon. The equipment included a mercury pressure transmitting device to keep the gas volume constant. At low temperatures a temperature gradient in the gas in the pressure transmitter could present difficulties. In addition, there was some gas volume which never came in contact with the adsorbent; this presents no difficulties when working with pure components but makes it impossible to use this apparatus for multicomponent adsorption studies.

The Present Apparatus

A schematic diagram of the system used in the present study can be found in diagram I. There are two large feed tanks (A), size 1A cylinders, which contain pure component. These are connected to the main feed reservoir (B), which is a high pressure vessel fabricated of 2 1/2-in. extra heavy-duty pipe and has a volume of about 940 cc. The feed reservoir is connected by a quarter inch high pressure line to the feed pressure gauge (C), and the distribution block. From the distribution block, lines lead to the sampling connection (D) and the vacuum and expansion system (E). A third line leads through the sampling connection (K), through the low temperature cell block valve (L), to the adsorption cell (F) which is discussed in greater detail below. The vacuum and

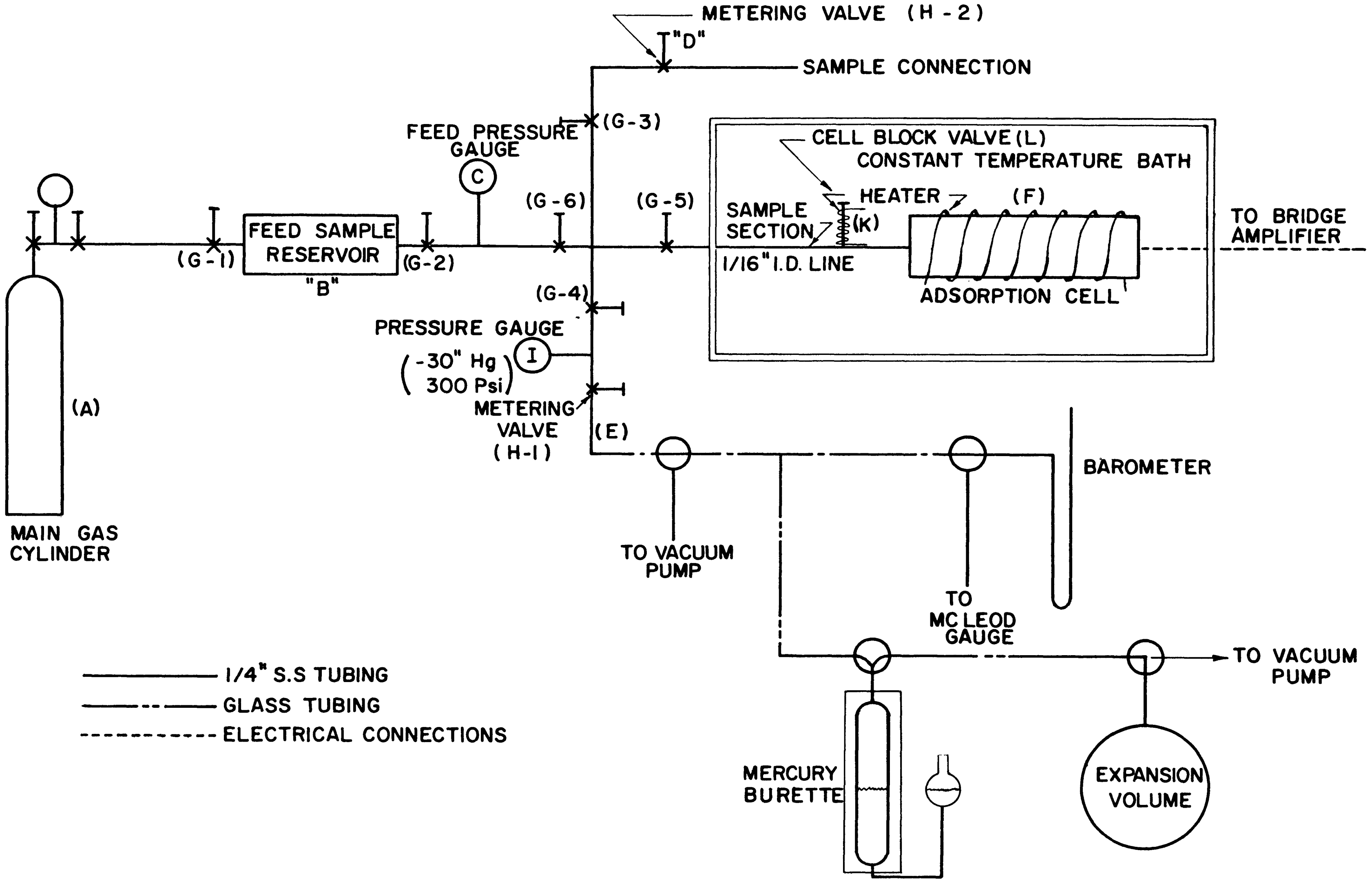


Figure 1. Flow Diagram of Adsorption Apparatus.

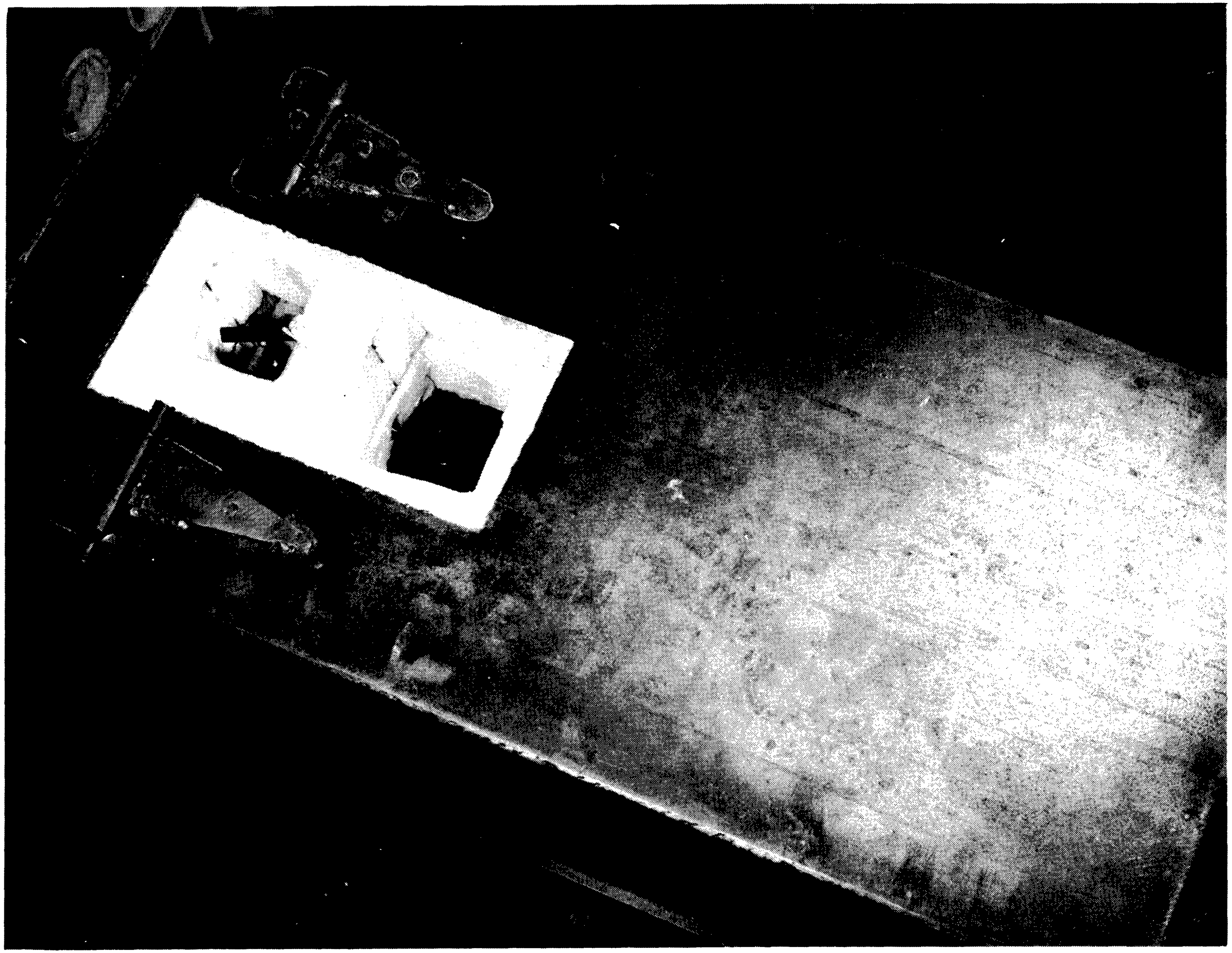


Figure 2. Top View of Closed Bath (showing protective steel shield).

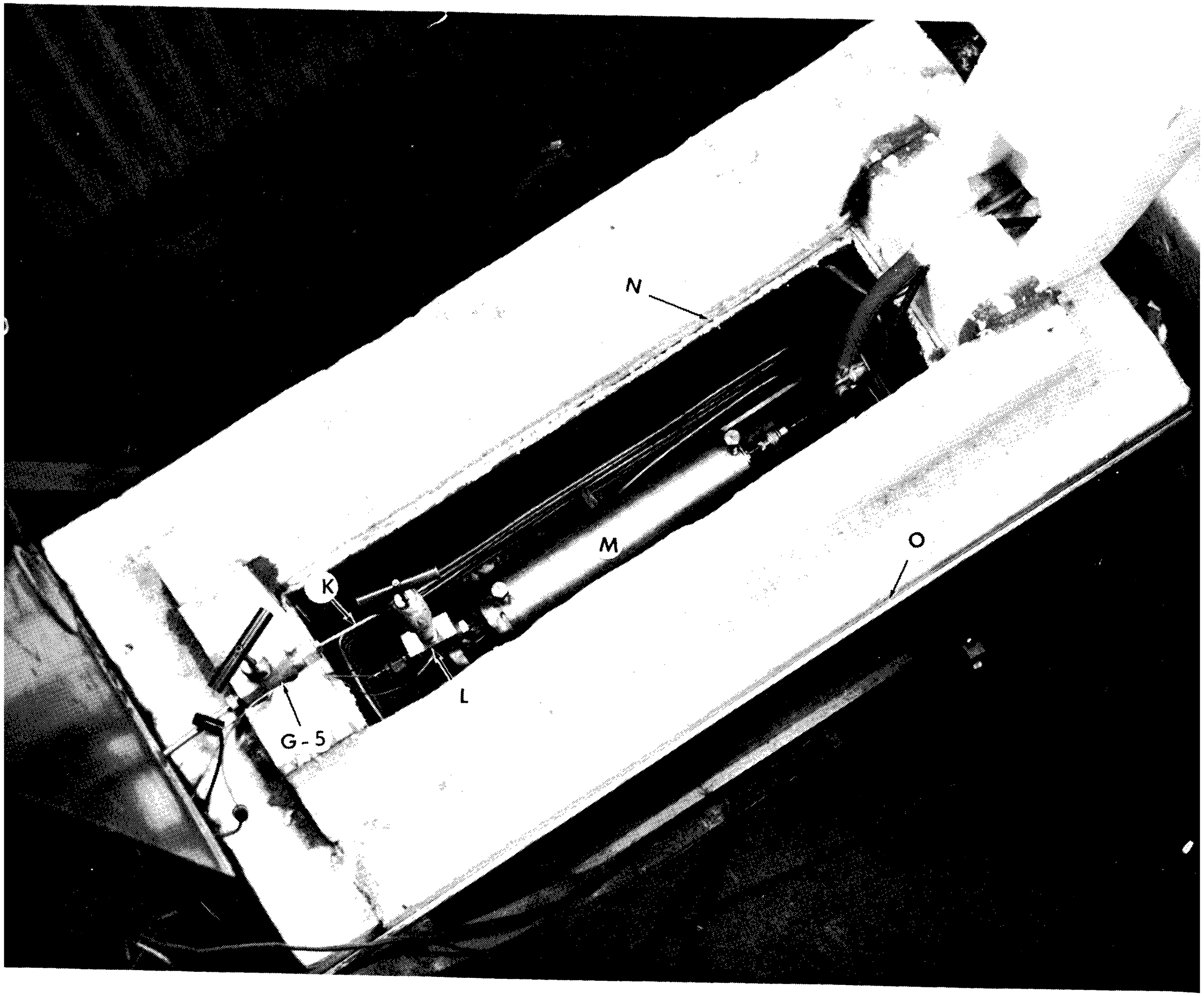


Figure 3. Open Constant Temperature Bath.

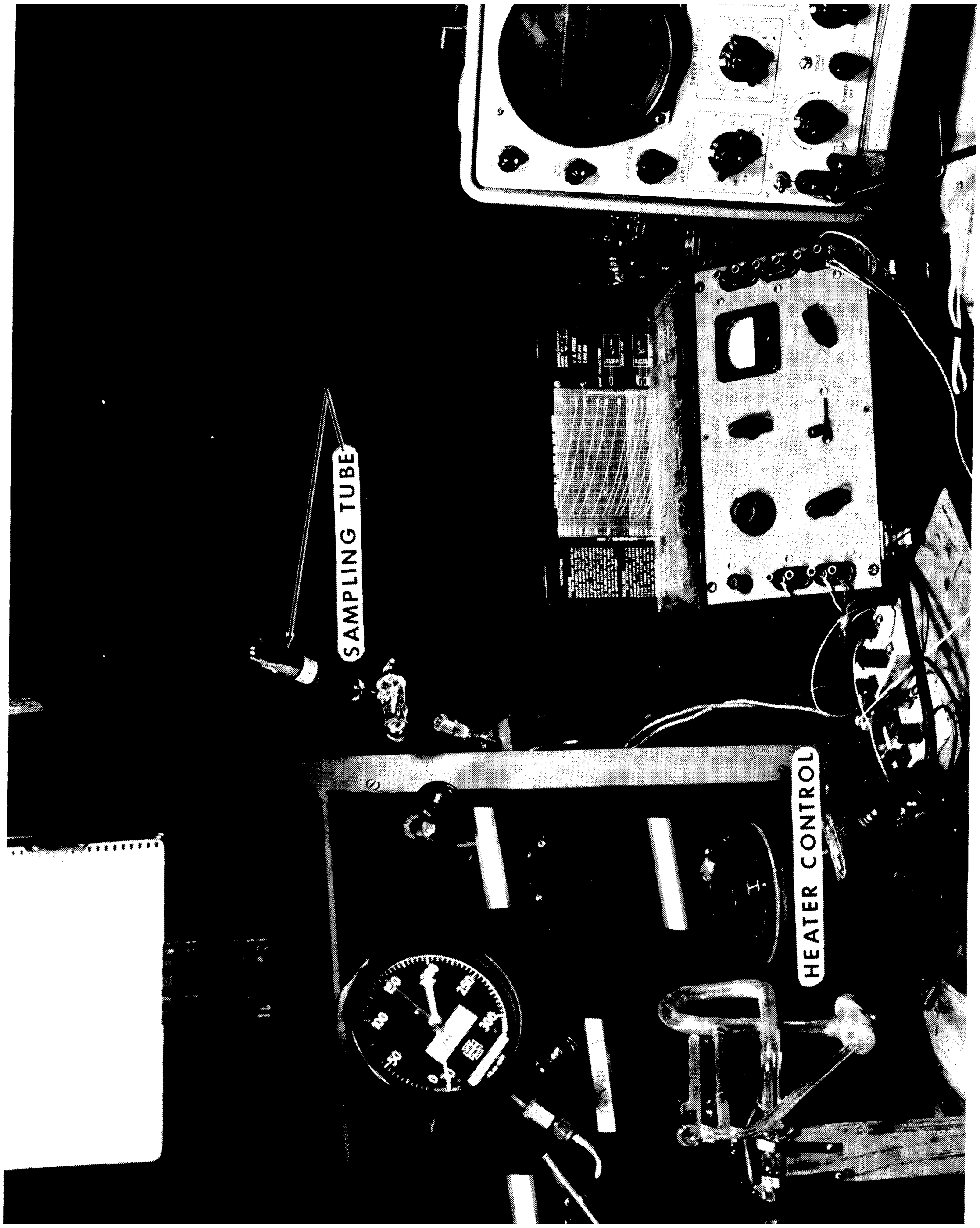


Figure 4. Instrument and Control Section.

expansion systems are made of glass and are protected against high pressure surges by standard Autoclave 10,000 psi. valves (G3, G4) and Hooke metering valves (H1, H2) in series. A low pressure gauge (I) is placed in between the block and metering values on the vacuum line as an additional precaution. The entire system is at room temperature except for the adsorption cell and cell sampling line (K) which are in the constant temperature bath.

The Adsorption Cell

The major modifications from other similar system were made to the adsorption cell. The cell, shown in detail in Figure 3, was made of 316 stainless steel and designed according to the ASME-API Code for Unfired Pressure Vessels.(2) Detailed design calculations may be found in Appendix D.

The two ends were machined from bar stock and the center cylinder is a piece of 1 1/2-in. schedule 180 seamless tubing donated by Babcock and Wilcox. The ends were joined to the cylinder using 308 stainless steel welding rod in order to prevent the formation of delta ferrite. The vessel was then x-rayed to insure the soundness of the welds. In order to release any stresses produced during welding or machining, the entire vessel was heat treated as 750-800°F for two hours and then furnace cooled.

The quarter inch tubing connects to the main block valve (L) and is fitted with a fine stainless steel screen to prevent particulate matter from fouling the valve. The thermocouple well is standard 1/8 inch high pressure tubing. The 18 mm. threaded aperture serves both for filling the vessel with adsorbent and as the connector for a

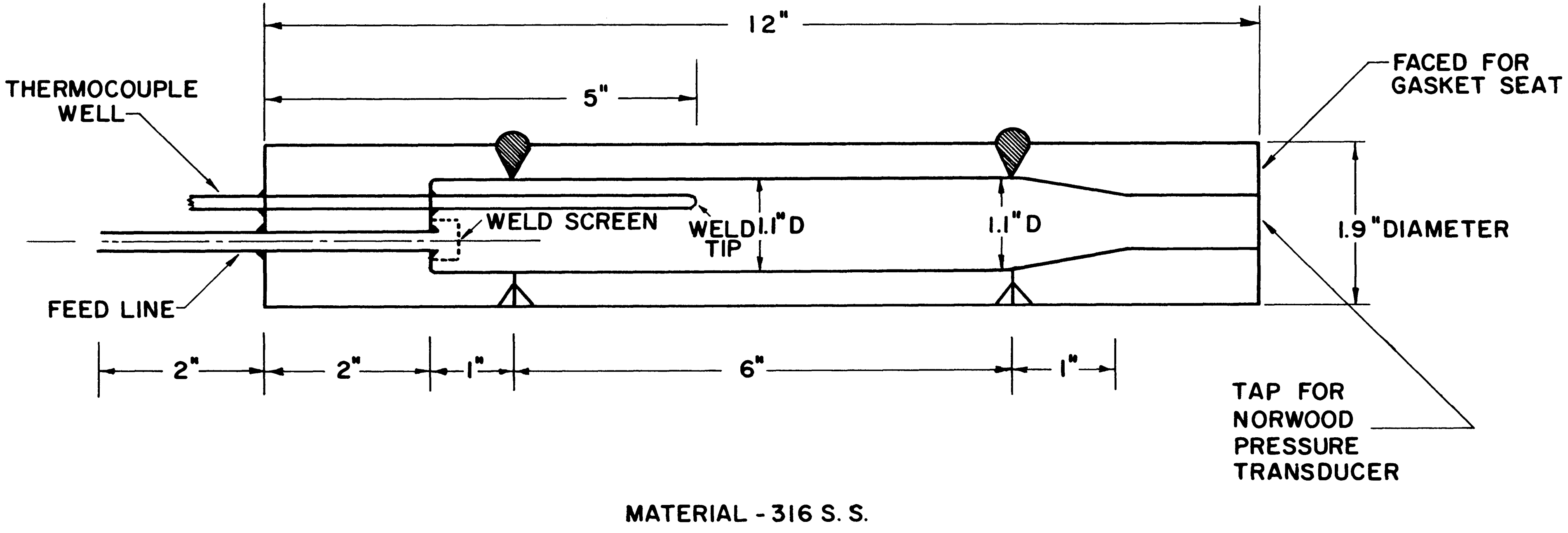


Figure 5. Adsorption Cell in Cross Section, (F).

pressure transducer used for determining the pressure in the cell. This end is faced for a gasket and a teflon gasket is used. Thirty foot-pounds torque is sufficient to seal the gasket and insure a tight system.

The use of a pressure transducer elminates the need for any long connections where gas not in contact with the adsorbent can collect. In order to further reduce any "dead" space the quarter inch outside diameter connecting line is filled with clean copper wire.

The cell sampling connection (K) is a length of 1/8 inch outside diameter tubing, also filled with copper wire so that the sample size can be kept to a minimum.

Thus, the main feature of this system is the low "dead" space, assuring good contact between the entire gas sample and the adsorbent.

The Pressure Transducer

Pressure transducers are basically strain gauge devices. Several manufacturers make a variety of these devices and the Norwood Controls Transducer Model 101, of which Figure 6 is a schematic diagram, was picked because of its ease of operation, good response and the wide choice of pressure ranges available.

The pressure signal is received by a diaphragm which compresses a strain tube which supports the center of the diaphragm. Any changes in the strain tube are immediately detected by two strain gauges, one wound circumferentially and the other longitudinally. The gauges stretch and shorten respectively with an increase in pressure.

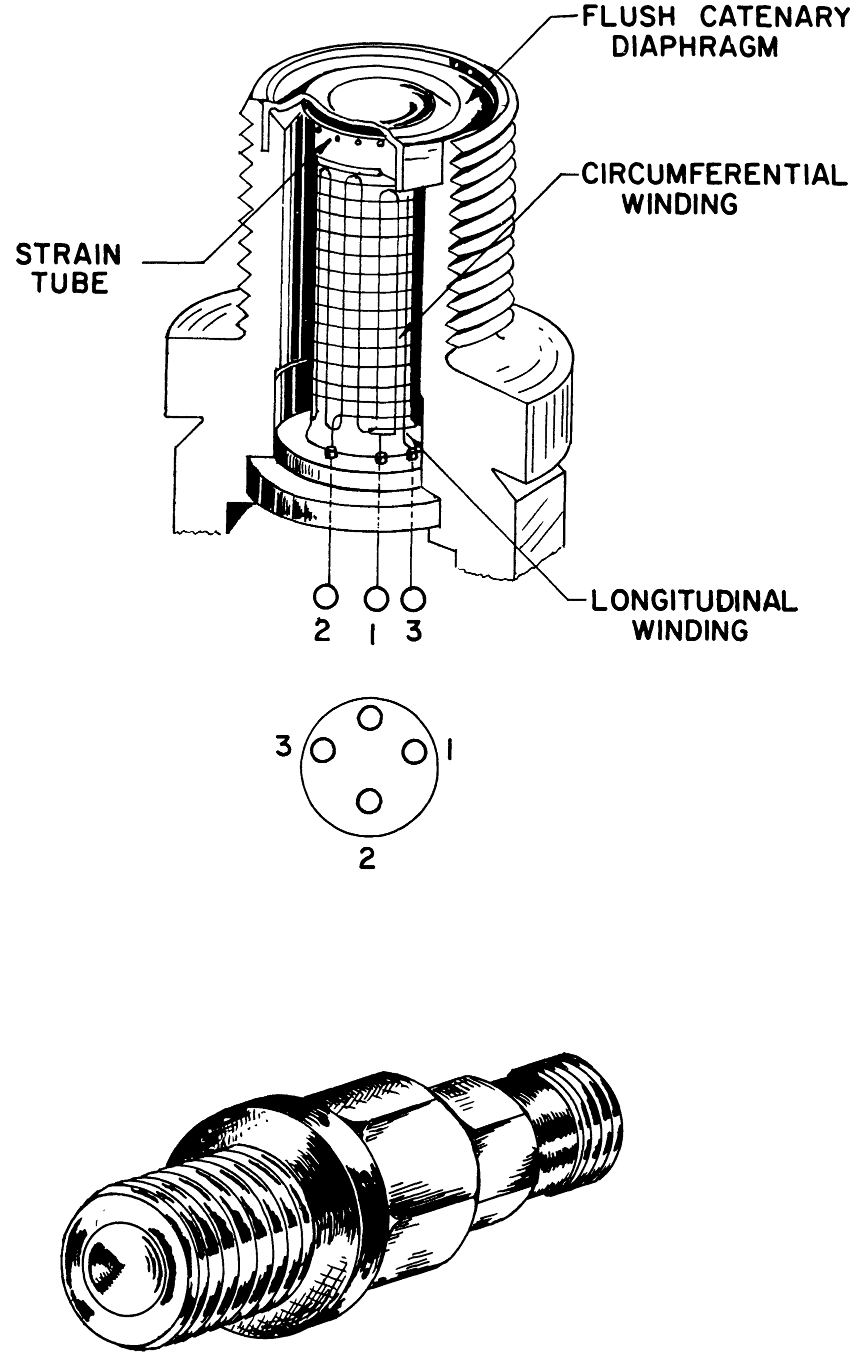


Figure 6. Schematic Diagram of Norwood Pressure Transducer.
Courtesy of Norwood Unit - Controls Division
American Standard Corporation.

The output produced by changes in the strain gauge is transmitted to an Ellis Bridge Amplifier which contains the other elements of the bridge circuit as well as an amplifier. The output signal from the amplifier is proportional to the induced strain and is read on a Model 130B Hewlett Packard Oscilloscope. The complete circuit including amplifier and scope are shown schematically in Figure 7.

TABLE I

NORWOOD PRESSURE TRANSDUCER SPECIFICATIONS

		-15 to 500 psig Transducer	-15 to 2000 psig Transducer
Accuracy	± 1% of rated pressure	±50 psi	±200 psi
Linearity	± 1% over entire range		
Resolution	0.1% of rated pressure	5 psi	20 psi
Repeatability	1/4% of full scale	12.5 psi	50 psi
Temperature Effect	0.02%/F may be balanced out at any given temperature		

The specifications listed in Table I and the calibrations found in Appendix B, clearly show that these transducers are acceptable as secondary pressure measuring devices, if used with a linear amplifier and sensitive display device such as the oscilloscope mentioned previously. There is, however, a very definite need to choose the range of the transducer carefully so that the rated pressure is not exceeded by fifty per cent and that the pressure to be measured is greater than ten per cent of the rated pressure. Within these bounds the transducer will perform most satisfactorily.

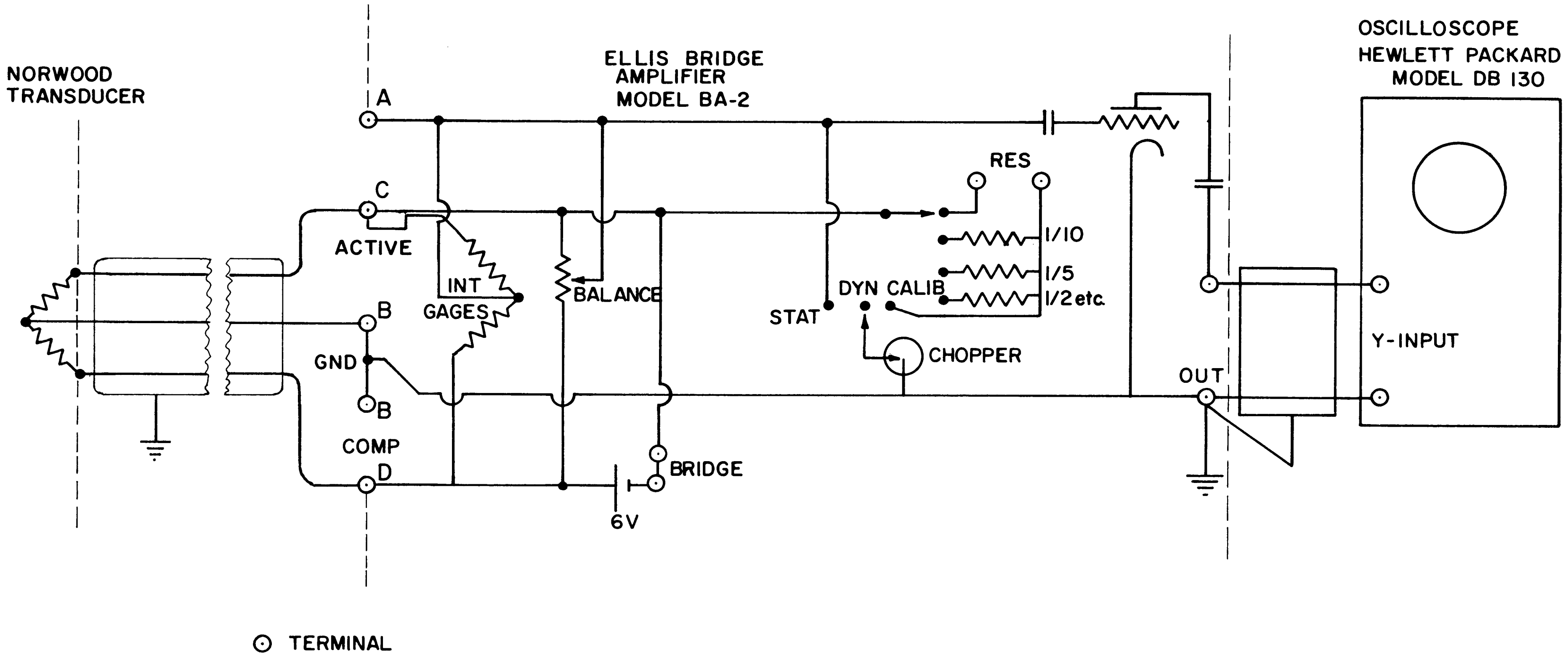


Figure 7. Simplified Schematic of Electrical Measuring Circuit.

In order to cover the desired range of pressures adequately, two transducers were used, a 2000 psi transducer and a 500 psi transducer.

Material Selection

As low temperature operation was anticipated, all high pressure lines, vessels and connectors were made of austenitic stainless steel. All welds were made with 308 rods to prevent delta-ferrite formation. Wherever possible, standard parts of 316 stainless steel were purchased. Special stainless steel packing washers and packing nuts, rather than the standard bronze parts, were used in the valves which were exposed to low temperature. All valve packings used in valves at low temperature were made of Dilecto, a glass impregnated with teflon. This material is dimensionally more stable than teflon and proved an excellent packing. Some difficulty was encountered at low temperature in the main block valve (L). This is discussed in some detail below.

The inner liner of the constant temperature bath is made of an 1/8 inch copper plate. The cooling coils were also constructed of copper. Around the copper tank there are six inches of Styrofoam insulation.

Valve Operation at Low Temperature

The operation of valves at extreme temperatures can present a problem. The basic problems encountered are the differences in thermal expansion of various metals and packings and the lack of good, low temperature lubricants.

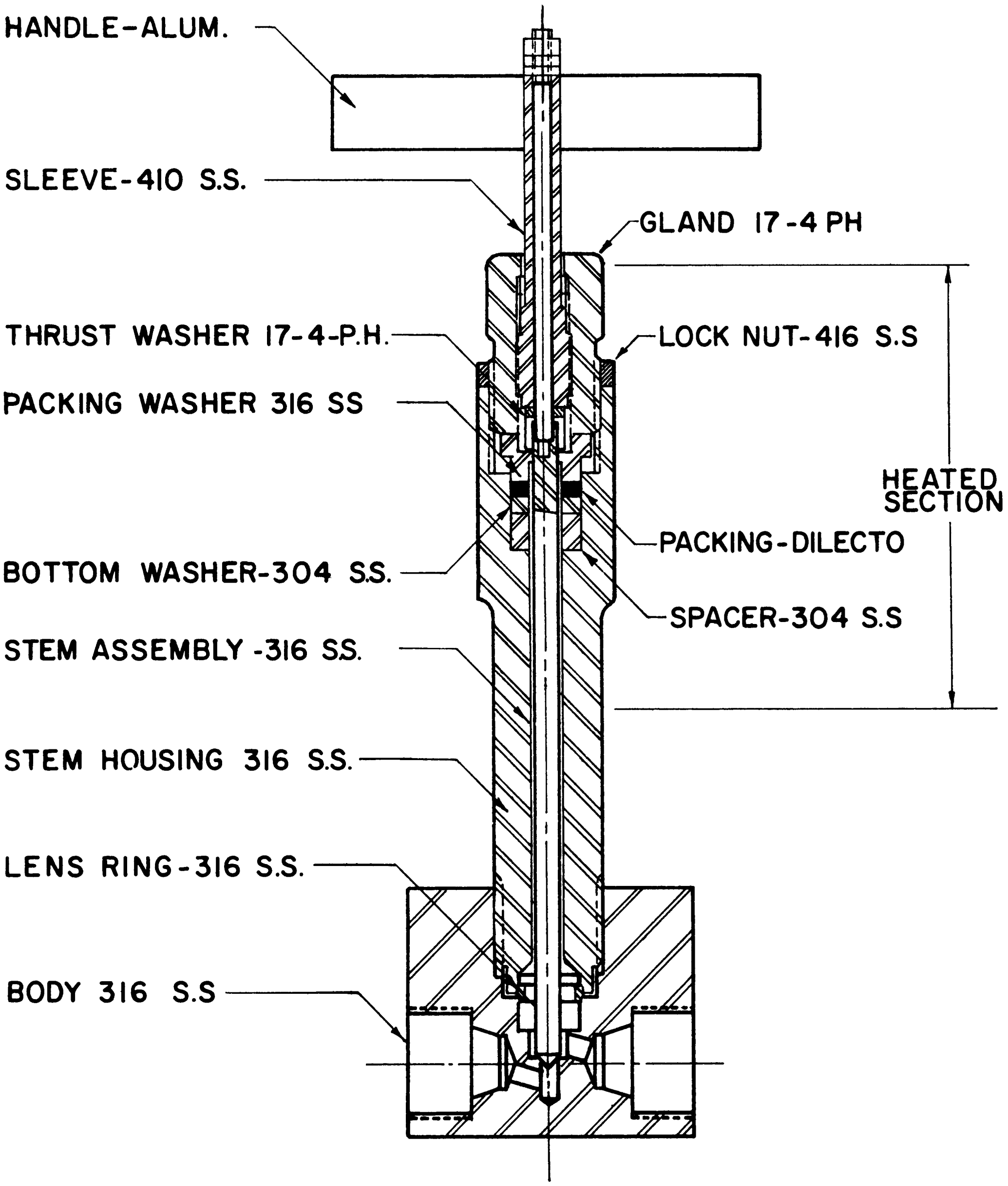


Figure 8. Cross Section of Main Block Valve (L).

Courtesy of Autoclave Engineers Inc.

A standard Autoclave high pressure valve with stainless steel used throughout proved unsatisfactory, possibly because of the incorrect choice of material as seizing occurred between the stem (420 stainless steel) and the bottom washer made of 17-4PH Armco steel.

A high temperature valve, Figure 8, was inserted and with several modifications worked well throughout the tests. This valve has a two piece stem, the sleeve of which is made of 410 stainless steel. At low temperatures, where it is very critical that all contacting parts be clean and dry, this sleeve tends to gall in the packing nut threads. In order to eliminate this problem the stem must be treated so that its surface has properties different from those of the packing nut. This may be accomplished by either nitriding the surface or putting on a surface film which can withstand low temperatures. Both methods were tried, the former by the Tufftride* process, and the latter with a coating of teflon about 0.002 inches thick. Both methods appeared to work well, although no extensive tests were made. During the course of the tests, the Tufftrided stem was used and the long stem was wound with a heater to keep the valve packing and gland nut at temperatures no lower than -100°C.

Temperature Measurement and Control

Temperature in the cell was measured with a thermocouple made of matched 30 gauge copper and constantan wire. A continuous record of the cell temperature was made and the recorded reading was checked periodically with a Leeds and Northrup Semi-Precision Potentiometer.

---

* Trademark of the Kolene Corporation.

Another copper-constantan thermocouple was attached to the outside of the cell. The output from this thermocouple was recorded by a Micromax recorder-controller. The control element was an on-off switch controller Skinner three way valve. This valve, when on, allowed gaseous nitrogen, under pressure, to force liquid nitrogen into the constant temperature bath. With the aid of a 192 watt heating element wound around the cell, and controlled by a Variac, temperatures could easily be kept at ± 0.5°C within the cell.

The temperature of the reservoir was measured with a copper-constantan thermocouple and Leeds and Northrup student type potentiometer. The temperature of the expansion volume and gas burette were determined with standard thermometers.

Temperatures taken with the thermocouples could be determined to ± 0.5°C under the most severe conditions, -192°C and within ± 0.1°C at ambient conditions. The thermometers could be read to ± 0.2°C.

Safety Considerations

Whenever experimental work is carried out at high pressures and extreme temperatures the safety of both personnel and equipment becomes an important consideration.

The adsorption cell, after welding, x-raying and stress relieving was hydraulically tested to 8,500 psi which was about one and a half times the design pressure. The entire high pressure system was then hydraulically tested at 7500 psi. In addition to the hydraulic testing, several safety shields were provided as can be seen in Figure 3. The inner shield (M) is a 2 1/2-inch schedule 80 stainless steel pipe with the end near the transducer closed, to provide a shield should the transducer fail. A 1/8 inch copper bath (N) provided additional protection. One quarter inch steel plate (O) served as a final shield with space for the gas to escape between the hinged cover and the fixed tank. The temperature of this shield was checked with the bath at liquid nitrogen temperature (-196°C) in order to insure that its temperature was above the brittle fracture temperature, about 30°F. The temperature was about 65°F with a room temperature of about 72°F.

A blow out disk was provided in the high pressure lines and was rated at 3,000 psi or one and a half times the maximum normal operating pressure.

In order to protect the glass vacuum system and sample bottles, a block valve (G) and a metering valve (H) were placed in series and the two were never opened together if the pressure upstream from the block valve exceeded two atmospheres.

These precautions have proved sufficient; to date no accident has occurred.

Leakage in the System

In a static system it is important that the test cell in particular be leak-free. In order to determine the leakage, if any, in the test cell, a series of pressure tests were conducted over a twenty-four hour period each. In addition, tests at vacuum were conducted in order to determine if any leakage at low pressure was present. The cell was also tested using the pressure method with a helium detector.

The high pressure tests were conducted at 2,000 psi. It was found that no visible leakage, as determined by readings on the pressure gauge, occurred in a twenty-four hour period. This would mean that any losses would be less than one part in a thousand during that period of test. This was deemed sufficient to consider the system free of any leakage. Vacuum tests were conducted on the cell. The cell was evacuated to a pressure of ten microns and was then closed. The rest of the system was kept under a vacuum of ten microns and after a period of eight, sixteen and twenty-four hours the pressure in the cell was determined. The pressure in the cell was found to be no greater than twenty microns after a twenty-hour period. This was considered sufficient to consider the cell free of any leaks.

The helium leak detector was used to find any possible small leaks. In this particular test the cell was filled with helium to a pressure of 2,000 psi and all joints were examined with the probe from the helium leak detector. No leakage indications were discovered.

The loading system was also checked for any leaks. This was done in a manner similar to the one used for the test cell. The duration of the tests, however, was only two and four hours. No leakage was found over that period of time as determined by readings taken on a pressure gauge. The vacuum system was tested for possible leaks and the leakage in this part of the system was found to be less than one micron per hour. This was considered satisfactory for the purposes of the experiment.

Calibration of Equipment

All vessels and lines, with the exception of the large expansion volume, were calibrated using the volume expansion method. Helium, as well as dry air, were used as the calibrating gases except in the free space determination in which only helim was used. The large expansion volume was calibrated by filling it with a measured amount of water. The calibrated volumes are listed in Table II. The effect of pressure and temperature on the cell volume is negligible. Complete calculations may be found in Appendix D.

Several pressure gauges were used in the study in order to cover adequately the range of pressures studied. The two feed pressure gauges, 0-800 psi and 0-2000 psi and the -30 to 300 psig were calibrated against a dead weight tester. The calibration curves may be found in Appendix B. The calibration data was subjected to regression analysis using a program developed for the Bendix G-15 computer after the method of Milne(47). A second order fit represented the data very well.

The pressure transducers, 2000 psi and 500 psi, were calibrated in the system against the pressure gauges. These data were also fitted with a regression curve of second order. The calibrations may be found in Appendix B. Excellent reproducibility was achieved at a given temperature range and although they are compensated for changes in temperature over part of the range, a change in the calibrations occurred over the range of interest. No drift in the calibrations occurred with time and it appeared, therefore, that the slight decrease in battery power had no effect on the readings.

TABLE II

CALIBRATED VOLUMES

Volume Calibrated	Volume CC.
Constant Volume Reservoir	923 ± 3.cc
Reservoir Connections	38.2 ± 1.cc
Central Distribution "T"	8.63 ± 0.1cc
Cell Sampling Line Section	2.46 ± 0.05cc
Vacuum Safety Gauge and Connections	12.7 ± 1.cc
Glass Lines (To top of barameter)	127.7 ± 5.cc
Barometer	0.196 ± 0.004cc
Expansion Volume	11,780cc ± 50.cc
Adsorption Cell-Filled-Free Space	
Runs 1-107	89.7 ± 0.7cc
Runs 107 -	88.8 ± 1.0cc

The thermocouple used to determine the cell temperature was checked against a nitrogen-filled pentane thermometer at the ice point, in dry ice, and in liquid nitrogen. At all three temperatures the readings checked within 0.5°C. As this was well within the accuracy of the equipment the temperatures recorded by the thermocouple were assumed to be accurate.

EXPERIMENTAL METHOD

Adsorbent

The adsorbent is a calcium substituted Aluminosilicate commercially known as Linde Molecular Sieve 5A. This material is similar to the natural zeolites, chabizite and analcite. Natural materials of this type and related synthetic zeolites were studied by Barrer and co-workers.(4)

The sieve used in this study has been studied in some detail by Breck and co-workers of the Linde Company. The basic chemical composition of the hydrated crystal is $Ca_6(AlO_2)_{12}(SiO_2)_{12}\cdot 3H_2O$.(12,53) The basic structure of the unit cell has been described as a framework of alumina (AlO_4) and silica (SiO_4) tetrahedra linked at their apexes, providing a large interior cavity linked to other cavities by eight sided and six sided passages. The edge of the tetrahedra form eight membered oxygen rings with a diameter of 5.0 to 5.6Å. In addition there are small six membered rings of approximately 3Å in diameter leading from the interior cavity.

The sieve is supplied in the form of 1/16 inch or 1/8 inch pellets and in this study the former were used. These pellets are about 80 per cent actual crystal. The remainder is binder. The sieve has a surface area of 500 square meters per gram (see Appendix C) as measured by the "BET" method and agrees with the data of Breck (12).

The adsorbent will rapidly adsorb water vapor upon exposure to the atmosphere. It is therefore necessary to activate the sieve before any equilibrium determinations are made. The recommended activation conditions are 350°C at one atmosphere or lower temperatures at lower pressures. The sieve used in these experiments was activated for a minimum of 12 hours at 175°C and at a pressure of 10^{-2} mm.Hg. Between individual equilibrium determinations, the adsorbent was held for 4 hours at 175°C and 10^{-2}mm Hg after nominally complete desorption had been achieved.

In order to determine the effect of regeneration temperature and pressure, the surface area was determined after desorbing samples of sieve at 300°C and 10^{-6} mm Hg. and at 125°C and 10^{-2}mm.Hg for eight hours. There was no significant difference; the specific surfaces of the samples (See Appendix C) were within three per cent of each other which is well within the accuracy of the method. In addition, a sample of the adsorbent which had been regenerated in the cell at the normal desorption conditions, 175°C, 10^{-2}mm.Hg for a minimum of 4 hours, was desorbed for 12 hours at 350°C. The weight difference was 1.45 grams per 100 grams of adsorbent, equivalent to about five per cent of the water capacity of the sieve.

Gases

The Methane used in this study was obtained through the courtesy of Phillips Petroleum Company in standard, seventy cubic cylinders at 2000 psi. The gas received was pure grade, 99 plus per cent methane. A number of analyses of the methane were made during the course of the study with the mass spectrometer. A typical analysis can be found in Table III.

The nitrogen used was prepurified grade nitrogen purchased from the Matheson Company in standard 220 cubic foot cylinders at 2000 psi. This gas is sold with a specification of 99.99 per cent nitrogen

TABLE III

ANALYSES OF PURE FEED GASES

Component	Per Cent	
METHANE		
Methane	98.6	98.7
Nitrogen	1.0	0.9
C_2^+	0.2	0.2
CO_2	0.2	0.2
H_2O	None Evident*	
NITROGEN		
N_2	99.9+	
H_2O	None Evident*	
O_2	None Evident**	

* No. 18 peak on mass spectrometer

** No. 32 peak on mass spectrometer

content and a maximum dew point of -96°C. Each cylinder was sampled and a mass spectrometer analysis made; a typical analysis can be found in Table III.

As both gases were essentially pure and free of water, they were used as received.

Experimental Method

Of the two basic experimental methods, dynamic or flow and static or batch, the latter is in many ways the easier to execute and was chosen as the method to obtain the equilibrium data. Besides avoiding some of the experimental difficulties, such as keeping flow rates constant and measuring both flow rates and composition accurately for the entire run, the static method is more economical in regard to material consumption.

After activation of the adsorbent which is discussed above, any number of adsorption-desorption cycles can be made. The gas mixture to be adsorbed is mixed in the constant volume reservoir. The mixture is allowed to come to equilibrium for 24 hours. This was found sufficient to provide a feed mixture of constant composition in the reservoir.

Before any run the adsorption cell is brought to the adsorption temperature and the initial pressure must be less than 0.02 mm. mercury. The pressure and temperature of the reservoir are then determined. The pressure transducer circuit is balanced so that at full vacuum the oscilloscope display shows a balanced bridge circuit.

The main block valve (G-4) and metering valve (H-1) to the vacuum system are closed and the main block valve from the reservoir (G-6) is opened. The cell is loaded with the gas mixture and the main cell valve (L) is closed. The pressure and temperature of the reservoir are again determined and a sample of the feed gas is taken for analysis.

The system is allowed to come to equilibrium. Temperature is recorded continuously during the run. At the beginning of any run, as the gas is admitted and adsorbed, the system temperature is above the equilibrium temperature. The system temperature, depending upon the conditions, will be as much as 50°C above the equilibrium temperature. Within 15 minutes, the temperature dropped to within five degrees of the equilibrium temperature. The equilibrium temperature is reached within one hour.

Periodic pressure readings are made during the run. The pressure decreases rapidly during the first fifteen minutes. The pressure normally will decrease to the equilibrium pressure within the first hour. In order to insure that equilibrium is achieved, at least eight hours is allowed. A series of tests over a longer period of time indicated that essentially no change in the gas phase occurred after four hours, the time the first sample was taken. After eight hours, two pressure readings taken half an hour apart, at constant temperature, must be identical before the system is said to be at equilibrium. At equilibrium, the cell pressure and temperature are recorded and a gas sample is taken for analysis.

The adsorbate is desorbed into the large, 11,780 cc., expansion chamber and the pressure, temperature, and composition determined. Desorption for purposes of material balance is said to be complete when the equilibrium pressure is less than 1 mm. Hg. It requires between three and six desorption steps to obtain essentially complete desorption. In order to speed this process, temperature cycling is used with a maximum temperature of 170°C. After the equilibrium pressure is below 1 mm., the system is evacuated further to an equilibrium pressure of 0.01 mm. Hg. at 170°C.

Sampling

For ease of construction, only one line connects to the adsorption vessel. A small, approximately 2.5 cc. sampling section exists between the main cell valve (L) and the first block valve (G-5). The main distribution system then connects with the sample outlet and the glass sampling tube connection.

In order to obtain a gas phase sample, a 2.5 cc. purge sample is first taken. The line is then evacuated and the sampling section block valve (G-5) is closed. The sample is then obtained by opening the main cell valve (L). It is expanded into the glass sample tube. It is imperative that a true gas sample be obtained. The total sample is about five per cent of the total gas phase. In several tests several samples were taken in rapid succession. As indicated in Table IV, there is no difference in samples taken in rapid order; thus it can be assumed that the sampling technique gives a representative sample of the gas phase. On the other hand, if some time, say 20 minutes, elapses between samples, a new equilibrium is being approached. The rapid sampling is also accompanied by a temporary drop in pressure which increases again to a new equilibrium value with time; this supports the opinion that the gas phase sample is a representative sample of the gas phase only.

The samples were analyzed on a Consolidated Electrodynamics Corporation Model 21-103B Mass Spectrometer. This instrument is said

TABLE IV

PAIRED GAS SAMPLES FROM ADSORPTION CELL TAKEN AS A FUNCTION OF TIME TO DETERMINE SAMPLING VALIDITY

Sample Number	Time	Mole Fractions CH_4	Mole Fractions N_2	Deviation from Aver. for CH_4 Analysis
P-289	8:00 AM	.6512	.3488	- 0.0049
P-290	8:20 AM	.6561	.3439	0.0049
P-318	9:55 AM	.1182	.8818	0.0007
P-319	10:00 AM	.1169	.8831	- 0.0007
P-340	7:20 AM	.5030	.4970	0.0010
P-341	7:25 AM	.5010	.4990	- 0.0010
P-266	2:15 PM	.1459	.8541	0.0000
P-267	2:18 PM	.1459	.8541	0.0000

\- - - - - - - - -

TABLE V

REPLICATE ANALYSES OF A SINGLE SAMPLE

Sample No.	Analysis Mole Fraction CH_4	Analysis Mole Fraction N_2	% Deviation From Average for CH_4 Analysis
P-570a	0.1731	0.8269	- 0.34
P-570b	0.1735	0.8265	- 0.12
P-570c	0.1744	0.8256	0.40

Mean 0.1737

\- - - - - - - - -

TABLE VI

REPLICATE SAMPLES FROM A UNIFORM MIXTURE

Sample No.	Analysis Mole Fraction CH_4	Analysis Mole Fraction N_2	% Deviation From Average for CH_4 Analysis
P-428	0.7100	0.2900	- 0.14
P-431	0.7112	0.2888	0.03
P-435	0.7113	0.2887	0.04
P-438	0.7115	0.2885	0.07

Mean 0.7110

St'd Deviation = 5.87×10^{-4}

\- - - - - - - - -

to be accurate to less than one-tenth of one per cent but replicate analysis of the same sample, found in Table V, indicate that the precision of 0.2 per cent can be expected with certainty. To determine the accuracy of analysis, a series of replicate samples were taken and analyzed. The results may be found in Table VI. This data also indicates that any given analysis is good to ± 0.002 mole fraction or 0.2 per cent.

Method of Calculating Adsorption Equilibrium

The adsorption equilibrium cannot be directly calculated from the experimental measurements, pressure, temperature, gas volume and composition. The amount actually adsorbed is the difference between the amount of gas admitted to the cell and the gas remaining in the free space of the adsorption cell at equilibrium and may be represented for a given component by:

$$N_i = (N_{I,i} - N_{F,i}) - N_{FS,i} \qquad (29)$$

Equation (29) may be rewritten in terms of volume, density and compositions:

$$N_i = (V_I\rho_I - V_F\rho_F)y_{I,i} - V_{FS}\rho_{FS}y_i \qquad (30)$$

but the density is some function of pressure, temperature and composition:

$$\rho = f(P,T,y) \qquad (31)$$

In the regions of low pressure and high reduced temperatures the ideal gas law will represent the P-V-T data adequately. At high pressures and lower temperatures the gas behavior cannot be adequately represented by the ideal gas law and some correction must be made. Therefore, a more complex equation of state or a compressibility factor must be used. Of these two methods, the equation of state lends itself to computer solution and was used here. Several equations of state have been developed to represent the experimental P-V-T data. Of these, the most adequate is the Benedict, Webb, Rubin equation, which is an empirical equation developed for hydrocarbons using eight constants(6,7) and is of the form:

$$P = RT\rho + C_1\rho^2 + C_2\rho^3 + C_3\rho^6 \qquad (32)$$

where

$$C_1 = B_oRT - A_o - C_o/T^2 \qquad (32a)$$

$$C_2 = (bRT-a) + C/T^2[(1+\gamma\rho^2)/e^{\gamma\rho^2}] \qquad (32b)$$

$$C_3 = a\alpha \qquad (32c)$$

The B-W-R equation as developed originally was intended to predict vapor-liquid equilibria of hydrocarbon mixtures. In the original work no constants for nitrogen were published. Bloomer and co-workers fitted a modified B-W-R equation of state for nitrogen.(10) The equation added two constants to better represent the data, changing the first and second virial coefficients, so that:

$$C_1 = B_oRT - A_o - C_o/T^2 - D_o/T^4 \qquad (32d)$$

$$C_2 = bRT - a + (\frac{C}{T^2} + \frac{\delta}{T^4})[(1+\gamma\rho^2)/e^{\gamma\rho^2}] \qquad (32e)$$

In later work, based on experimental data of Sault(54), Darby,(17) Pace,(44) and Keyes and Burks(34) for nitrogen-methane mixtures, Ellington and co-workers(19) recommended the following combinatorial rules for the ten-constant modified B-W-R equation:

$$B_{om} = \sum_i x_iB_{oi} \qquad (32f1)$$

$$C_{om} = (\sum_i x_iC_{oi}^{1/2})^2 \qquad (32f2)$$

$$D_{om} = (\sum_i x_i D_{oi}^{1/2})^2 \qquad (32f3)$$

$$a_m = (\sum_i x_i a_i^{1/3})^3 \qquad (32f4)$$

$$b_m = (\sum_i x_i b_i^{1/3})^3 \qquad (32f5)$$

$$c_m = (\sum_i x_i c_i^{1/3})^3 \qquad (32f6)$$

$$\alpha_m = (\sum_i x_i \alpha_i^{1/3})^3 \qquad (32f7)$$

$$\gamma_m = (\sum_i x_i \delta_i^{1/3})^3 \qquad (32f8)$$

with a special modification for the constant A_o:

$$A_{om} = (\sum_i x_i A_{oi}^{1/2})^2 - 0.1000\ (X_{N_2} \times X_{CH_4}). \qquad (32f9)$$

The equation, as modified, represents data with an average deviation under one per cent at pressures up to 1500 psi and temperatures as low as -135°C.

As this equation is explicit in pressure, it is necessary to solve for the gas density by an iterative procedure. The Newton-Raphson method suits itself ideally to obtaining a solution rapidly in this case. In addition, the equation may be modified so that the fugacity of a gas may be computed.

Once the density is determined, the amount of each constituent in each phase can be readily determined, using relationship (30). The relative volatility can then be obtained from its definition:

$$\alpha = (y_{N_2}/X_{N_2})/(y_{CH_4}/X_{CH_4}) \qquad (33)$$

As part of the calculations necessary to obtain the equilibrium loading are iterative and lengthy, the entire calculation was programmed for the IBM 704 computer utilizing the MAD translator. The logical flow sheet, together with a sample calculation may be found in Appendix D.

Errors in Measurement

Two basic methods for error analysis exist. The first and perhaps most often used is statistical in nature and depends on the basic assumption that the measurements are Gaussian-distributed about the true value. In order to get a good measure of the errors, which are propagated in the results, a number of values of the result are necessary at a given parameter or it is necessary to assume a model for the data.

The second method of evaluating the effect of errors in measurement on the results is to determine the effect of the maximum possible errors in measurement on the calculated results. This method will bound the maximum error and in all but a very few cases the error in the finally calculated result will be measurably less that the maximum indicated from this type of analysis.

The second or maximum propagated error method has been used in analyzing the effect of errors in measurements on the results. In determining equilibrium values it is important that the degree of accuracy of the results be known with some certainty. This could be achieved by obtaining data for a number of runs at a given set of conditions, but it is often uneconomical to carry out this number of experiments. A more realistic approach, therefore, is to make only a single run at most conditions and obtain results over a wider range of the test parameters.

It is then best to make the error analysis by the second method unless one can assume a model which suits itself readily to a statistical regression analysis.

The maximum errors in the various measured variables are listed in Table VII. The maximum errors were determined by checking the values read against primary standard values or secondary standard values. In addition, the errors in reading due to parallax and other factors were taken into consideration.

In order to determine the effect of the maximum errors in measurements, the values used in a number of calculations covering the spectrum of results and basic data were altered. These altered data were then used to compute results using the basic computer program discussed above. The results obtained were then compared with the results obtained using the original data.

The conclusions of the error analysis may be found in Tables VIII and IX. The major effect on the calculated equilibria ensues from inaccuracies in the measurement of the feed pressures. This occurs because a relatively small net pressure is the difference between two rather large pressure values; thus small errors in the initial or final feed cell pressure can materially effect the total cell loading. The calculations indicate that the other errors in measurement propagate errors which are quite reasonable. The errors resulting from inaccuracies in the feed pressure determination should be well below the maximum as both pressures are read with the indicated pressure decreasing and within five minutes of each other. Any reading errors, therefore, should be in the same direction.

TABLE VII

ACCURACY OF MEASURING DEVICES

Measuring Device	Accuracy	% Error of Max Reading	Min Reading
2000 psi Pressure Gauge (500-2000 psi)	± 5 psi	0.25	1.0
800 psi Pressure Gauge (100-800 psi)	± 2 psi	0.25	2.0
2000 psi Pressure Transducer (600-2000 psi)	± 20 psi	1.0	3.33
500 psi Pressure Transducer (700-100 psi)	± 5 psi	0.7	5.0
Temperature (Thermocouple) (123°K-300°K)	± 0.5°K	0.5	0.16
Temperature (Thermometer) (300°K)	± 0.5°K	0.16	0.16
Mass Spectrometer Composition Analysis (Mole Frac.)	± 0.002		

TABLE VIII

MAXIMUM ERROR PROPAGATED IN PURE COMPONENT EQUILIBRIUM DATA

Measurement	% Changed	Milligram Moles Adsorbed	% Deviation
Original Run (Run 26)		0.266	0
Feed Pressure	0.5	0.258	3
Feed Volume	1	0.265	0.5
Cell Pressure	3	0.260	2
Cell Temperature	0.2	0.267	0.5
Cell Volume	1	0.265	0.5

\- - - - - - - - - - -

TABLE IX

MAXIMUM ERROR PROPAGATED IN BINARY EQUILIBRIUM DATA

Measurement	% Changed	Milligram Moles CH_4 Adsorbed	% Deviation
Original (Run 108)		0.0348	
Feed Pressure	2	0.0338	3.0
Feed Volume	1	0.0356	1.8
Cell Pressure	4.0	0.0350	0.6
Cell Pressure	4.0	*	0.7
Cell Composition	1.3	0.0349	0.3
Cell Volume	1.0		
Cell Pressure,	4.0		
Composition	1.3	0.0350	0.57
and Temperature	0.16		

* Total adsorption

\- - - - - - - - - - -

The amount adsorbed should be within three per cent of the true value under all but the most unusual cases but even in these cases the value will be correct to plus or minus six per cent. The values of relative volatility in all cases are within six per cent of the true value.

EXPERIMENTAL RESULTS

Pure Component Adsorption

Pure component isotherms were obtained for methane at three temperatures and over a wide pressure range. Well above the critical temperature of methane at 295°K, nine equilibrium determinations were made up to 50 atmospheres or 760 psia. At 195°K, close to the critical temperature, nine determinations covered a pressure range of about 30 to 450 psia. Below the critical temperature, at 175°K, the equilibrium loading was evaluated at four pressures covering the range of pressures up to the saturation pressure. A tabulation of these results may be found in Table X. As discussed in detail below, the maximum error in any individual determination of the amount adsorbed is plus or minus four per cent. A statistical regression analysis of the data indicates that the isotherms are accurate to plus or minus five per cent 95 per cent of the time at the pressure extremes. The isotherms may be found in Figure 9.

Twenty-one values of pure nitrogen equilibrium loading, or amount adsorbed, were obtained. These may be found in Table XI. The isotherms were determined at 295°K, 195°K and below the critical temperature of nitrogen, at 123°K. At the higher temperatures, data was obtained at pressures up to 1300 psi and 900 psi respectively. Below the critical, the amount adsorbed was determined up to the saturation pressure. The 95 per cent confidence limits on the extremes of the adsorption isotherms, which may be found in Figure 10, are plus or minus five per cent.

The experimental data from which the equilibrium calculations were made may be found in Appendix A.

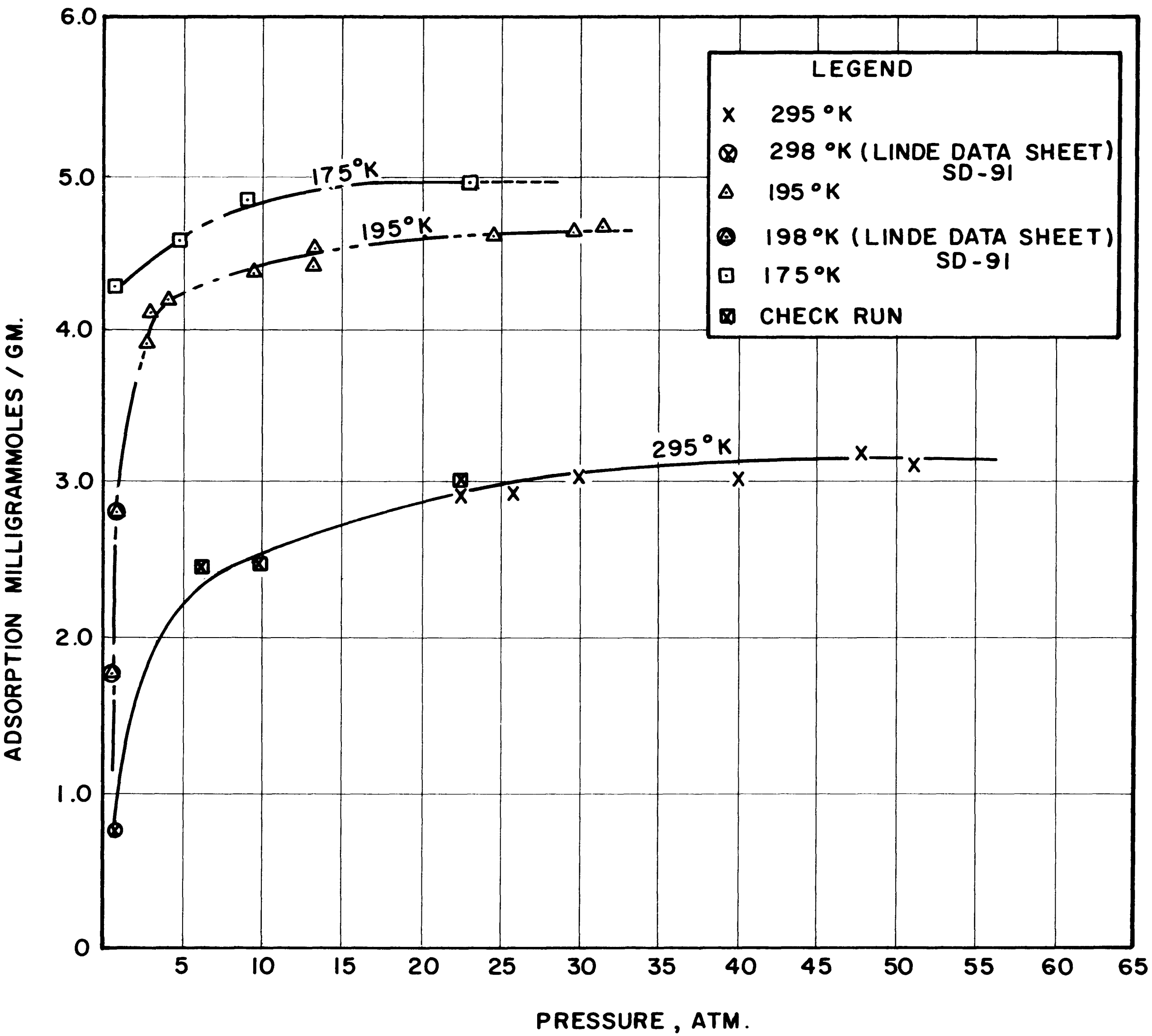


Figure 9. Methane Adsorption Isotherms on 5A Molecular Sieve.

TABLE X

PURE METHANE ADSORPTION

Run No.	Pressure ATM.	Temperature °K	Amount Adsorbed Milligram Moles/GM
	Average Temperature: 295°K		
115	51.3	297.0	3.12
25-1	47.63	293.0	3.24
26	40.15	297.0	3.01
27	29.94	296.0	3.05
28	25.86	295.5	2.91
122	22.5	296.0	3.02
25-2	22.46	293.0	2.94
124	9.78	296.5	2.46
123	6.40	296.0	2.52
	Average Temperature: 195°K		
114	31.30	195.5	4.70
52	29.70	196.0	4.61
56	24.84	194.0	4.56
58	13.13	195.5	4.39
92	9.25	193.0	4.34
53	9.08	195.5	4.66
57	3.54	195.5	4.17
93	2.93	193.0	4.12
59	2.72	195.0	3.92
	Average Temperature: 175°K		
78	22.52	175.5	4.95
79-1	8.98	174.5	4.83
79-2	4.87	174.0	4.62
80	0.50	175.0	4.25

- - - - - - - -

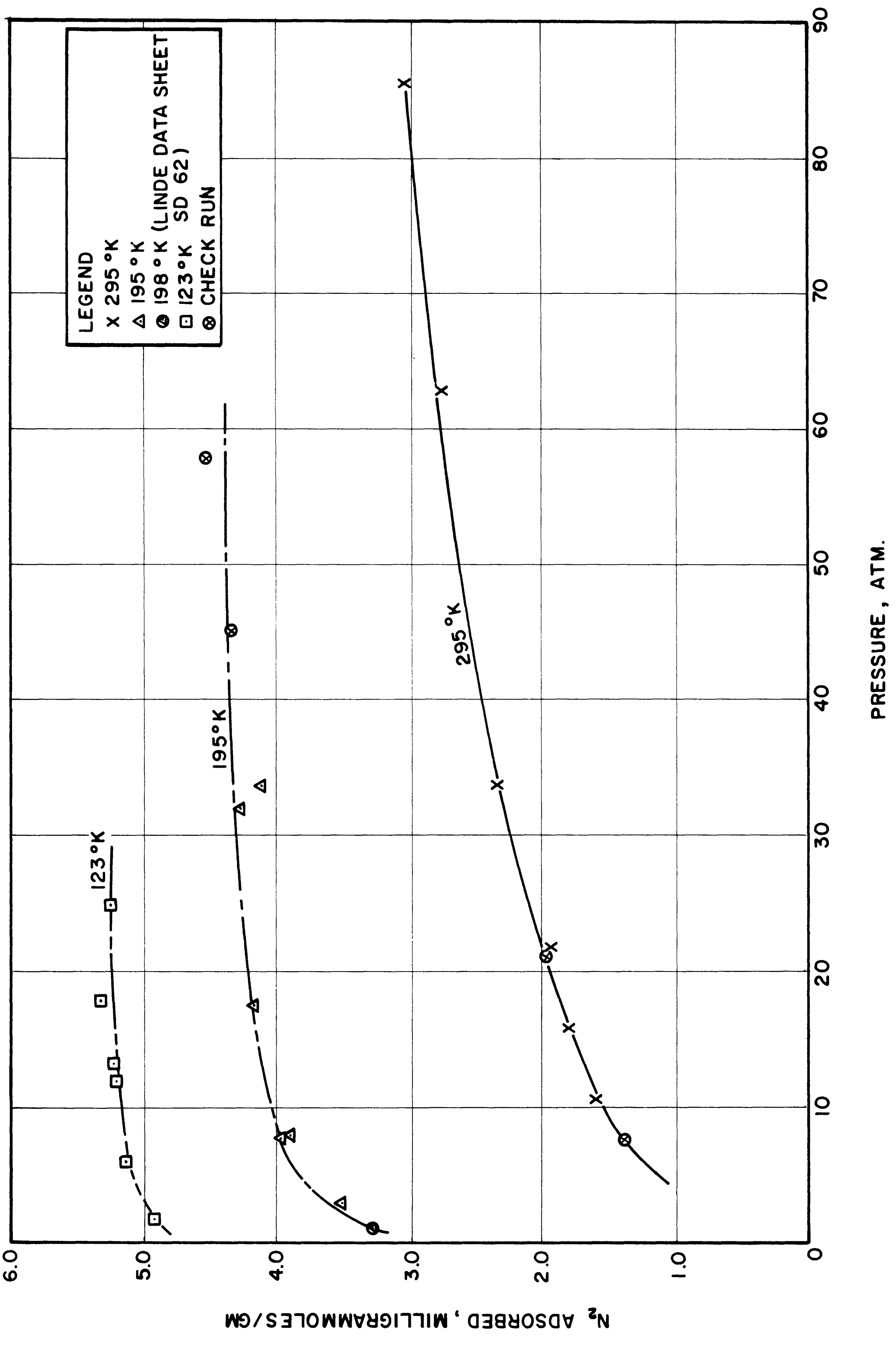


Figure 10. Nitrogen Adsorption Isotherms on 5A Molecular Sieve.

TABLE XI

PURE NITROGEN ADSORPTION

Run No.	Pressure ATM.	Temperature °K	Amount Adsorbed Milligram Moles/GM
	Average Temperature: 295°K		
29	85.4	294.0	3.06
30	62.9	295.5	2.74
31	33.68	295.0	2.32
32	21.57	295.5	1.92
120	21.3	295.5	1.95
33	15.65	296.0	1.80
103	10.55	296.0	1.66
121	6.78	295.0	1.39
	Average Temperature: 195°K		
112	57.84	195.5	4.54
113	44.91	195.5	4.35
71	33.48	195.0	4.12
51	31.98	195.0	4.31
72	17.56	194.0	4.16
73	7.72	194.0	3.90
74	2.86	194.0	3.54
	Average Temperature: 123°K		
84	24.82	123.0	5.24
85	17.60	123.5	5.30
87	13.34	123.0	5.23
86	11.64	123.0	5.19
88	5.78	123.0	5.14
89	1.59	123.0	4.93

\- - - - - - - -

Lewis(27) reported very limited data on methane adsorption on Davison Silica Gel and Columbia G Activated Carbon. The data indicate that the Molecular Sieve has a greater capacity for methane. Antropff(1) studied the adsorption of nitrogen on a Bayer-Werk Leverkusen activated charcoal. The data show that his particular adsorbent has a slightly higher capacity for nitrogen; for example, at 0 °C and 27 atmospheres it adsorbs 2.7 milligram moles per gram as opposed to the 2.2 milligram moles per gram capacity of the Molecular Sieve at 22 °C and 27 atmospheres pressure.

Binary Adsorption

Adsorption equilibria for mixtures of methane and nitrogen were evaluated at the four temperatures at which pure isotherms were determined, 295 °K, 195 °K, 175 °K and 123 °K. At the higher two temperatures, equilibrium adsorption was determined at pressures as high as 1350 psi or 90 atmospheres and gas phase compositions ranging between ten and ninety per cent. Results for the sixty runs may be found in Tables XII and XIII. Just below the critical temperature of pure methane, at 175 °K, the equilibrium loading increased from 4.75 to 5.04 milligram moles per gram of adsorbent with an increase of pressure from 7.6 to 30 atmospheres. The equilibrium amounts of each component adsorbed may be found in Table XIV.

At 123 °K, near the critical temperature of pure nitrogen, the quantity adsorbed was determined up to 300 psia for an equilibrium gas mixture containing five per cent methane.

The maximum pressure investigated was limited at the higher two temperatures by the cylinder pressure without any additional compression. At the lower two temperatures the dew point pressure was the upper pressure limit.

TABLE XII

MIXED ADSORPTION AT 295°K AVERAGE TEMPERATURE

Run No.	Pressure ATM.	Mole Fraction CH$_4$ Gas Phase	Amount Adsorbed Milligram Moles/GM			Relative Volatility
			N_T	N_{CH_4}	N_{N_2}	
13-1	89.82	0.793	3.27	2.61	0.68	2.2
13-2	89.82	0.802	3.09	2.48	0.61	2.31
13-3	83.02	0.787	3.30	2.60	0.70	2.08
13-6	57.16	0.790	3.33	2.63	0.70	2.16
13-9	42.19	0.793	3.22	2.55	0.67	2.14
13-11	30.28	0.818	3.19	2.61	0.58	2.46
14-1	76.21	0.639	3.45	2.66	0.79	1.91
14-2	74.85	0.633	3.45	2.68	0.77	2.02
15-1	28.58	0.593	2.70	2.04	0.66	2.12
15-2	27.90	0.544	2.70	2.10	0.60	2.94
16-2	14.29	0.590	2.36	1.74	0.62	1.94
17-2	90.84	0.161	3.08	0.87	2.21	2.06
17-4	61.92	0.161	3.16	0.88	2.28	2.02
17-5	59.98	0.168	3.18	0.87	2.31	1.87
18	47.29	0.155	2.86	0.74	2.12	1.91
19	22.80	0.146	2.05	0.53	1.53	2.03
20	74.85	0.705	3.51	2.94	0.57	2.15
21	56.14	0.700	3.00	2.50	0.50	2.14
22	34.02	0.675	2.83	2.29	0.54	2.05
23	24.50	0.667	2.38	1.94	0.44	2.19
24	15.31	0.656	2.02	1.62	0.40	2.15
104	30.62	0.271	2.86	1.28	1.58	2.16
105	21.71	0.274	2.56	1.10	1.46	2.00
106	9.12	0.270	1.89	1.78	1.11	1.90
107	21.07	0.150	2.41	0.60	1.81	1.89
108	8.39	0.149	1.75	0.39	1.36	1.66
109	35.40	0.171	2.90	0.86	2.04	2.03
110	19.64	0.173	2.31	0.67	1.64	1.94
111	12.83	0.174	2.13	0.60	1.53	1.85

- - - - - - - - - -

TABLE XIII

MIXED ADSORPTION AT 195°K AVERAGE TEMPERATURE

Run No.	Pressure ATM.	Mole Fraction CH_4 Gas Phase	Amount Adsorbed Milligram Moles/GM N_T	N_{CH_4}	N_{N_2}	Relative Volatility
34-1	84.04	0.150	4.44	1.55	2.89	3.03
34-2	81.65	0.153	4.54	1.55	2.99	2.86
35	46.61	0.120	4.50	1.40	3.10	3.30
36	28.92	0.110	4.34	1.26	3.08	3.29
37	16.47	0.112	4.18	1.18	3.00	2.93
39	47.63	0.606	4.29	3.53	0.76	3.04
40	28.58	0.556	4.25	3.45	0.80	3.44
41	11.36	0.503	3.50	2.64	0.85	3.36
43	37.43	0.405	4.51	3.08	1.43	3.20
44	16.33	0.406	4.28	2.98	1.30	3.40
45	76.89	0.476	4.80	3.20	1.60	2.21
46	36.74	0.611	4.30	2.78	1.52	2.88
48	18.17	0.451	4.18	2.98	1.20	3.02
61	6.51	0.314	4.10	2.22	1.88	2.58
62	1.97	0.334	3.75	1.97	1.78	2.21
64	20.48	0.121	4.23	1.18	3.05	2.81
65	7.59	0.126	4.07	1.03	3.04	2.36
66	1.38	0.133	3.42	0.83	2.59	2.69
67	31.20	0.546	4.75	3.72	1.03	2.71
68	16.40	0.531	4.96	3.74	1.22	2.70
69	7.96	0.508	4.36	3.21	1.15	2.69
70	0.95	0.542	3.54	2.53	1.01	2.34
94	33.4	0.201	4.33	1.89	2.44	3.05
95	13.27	0.176	4.19	1.59	2.60	2.87
96	4.76	0.188	3.92	1.40	2.52	2.42
97	28.58	0.357	4.63	2.91	1.72	3.05
98	19.53	0.334	4.44	2.67	1.77	3.03
99	6.98	0.326	4.13	2.30	1.83	2.74
100	24.36	0.687	4.60	3.96	0.64	2.76
101	13.98	0.658	4.55	3.86	0.69	2.92
102	4.49	0.700	4.21	3.46	0.75	1.95

- - - - - - - - - - -

TABLE XIV

MIXED ADSORPTION AT 175°K AVERAGE TEMPERATURE

Run No.	Pressure ATM.	Mole Fraction CH_4 Gas Phase	Amount Adsorbed Milligram Moles/GM N_T	N_{CH_4}	N_{N_2}	Relative Volatility
75	30.55	0.807	5.04	4.07	0.97	3.04
76	7.60	0.754	4.75	3.59	1.16	3.18
118	17.08	0.786	4.90	3.85	1.05	3.10

TABLE XV

MIXED ADSORPTION AT 123°K AVERAGE TEMPERATURE

Run No.	Pressure ATM.	Mole Fraction CH_4 Gas Phase	Amount Adsorbed Milligram Moles/GM N_T	N_{CH_4}	N_{N_2}	Relative Volatility
81	11.80	0.050	5.03	1.07	3.96	5.20
82	1.27	0.050	5.02	0.92	4.10	4.30
90	18.98	0.051	5.16	1.28	3.88	6.10
91	5.99	0.047	5.07	1.03	4.04	5.02

The individual determinations of the binary adsorption equilibria have a maximum error of plus or minus six per cent. It is apparent from Figure 11, which shows the total adsorption for the binary system, that the total equilibrium amount adsorbed is independent of composition. The 95 per cent confidence of these isotherms at their extreme is seven per cent.

TABLE XVI

CONFIDENCE LIMITS ON EQUILIBRIUM VALUES

	95 Per Cent Confidence on Isotherms at Pressure Extremes
Methane	5%
Nitrogen	5%
Methane-Nitrogen Mixtures	7%

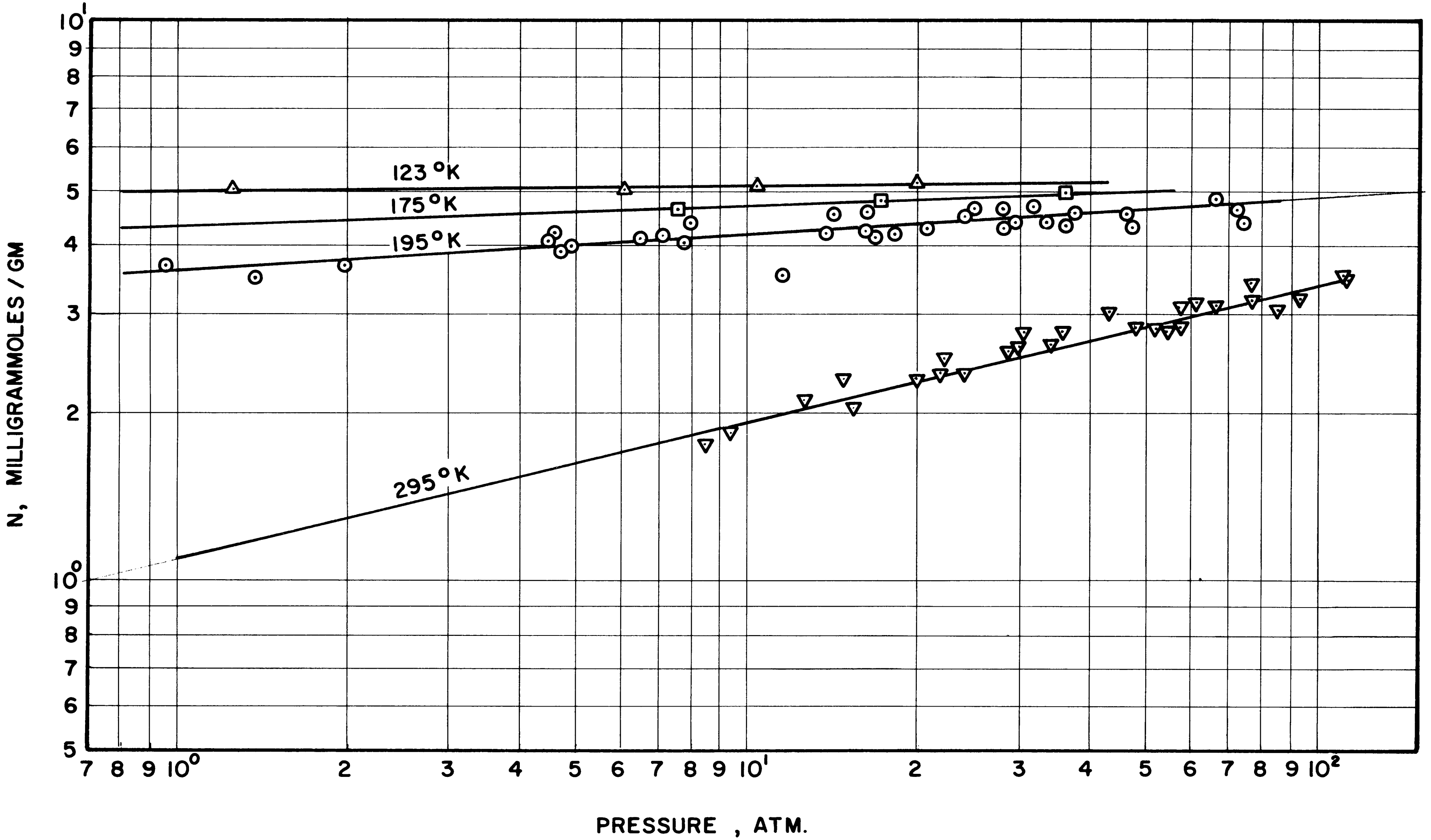


Figure 11. Mixed Adsorption as a Function of Pressure and Temperature.

DISCUSSION OF RESULTS

Pure Component Adsorption Correlations

A number of methods of correlating the data were tried in order to extend the usefulness of the data over the entire range of interest.

For pure component adsorption, both methane and nitrogen, the data was correlated using both the Freundlich

$$N = KP^{1/n} \tag{3}$$

and Langmuir

$$N = \frac{aP}{1 + bP} \tag{1a}$$

relationships as previously discussed. The constants for the correlations were obtained by the method of least-squares which is well detailed in standard references on numerical methods such as Milne.(47)

A plot of the experimental results for the pure components after Freundlich may be found in Figure 12. A Langmuir plot of the results has not been included but this would be rather easily constructed by plotting "P/N" in atmospheres per milligram mole per gram versus "P" in atmospheres. The constants, valid between 100 and 300° Kelvin, for the Freundlich equation are shown as a function of temperature in Figure 13, while those necessary to complete the Langmuir relationship may be found in Figure 14. Analytical relations for the Langmuir constants as a function of temperature will also be found with the graphical representation. The dependence of the constants on temperature is quite similar to that found by Fowler and Guggenheim(20) in their statistical development of the Langmuir equation.

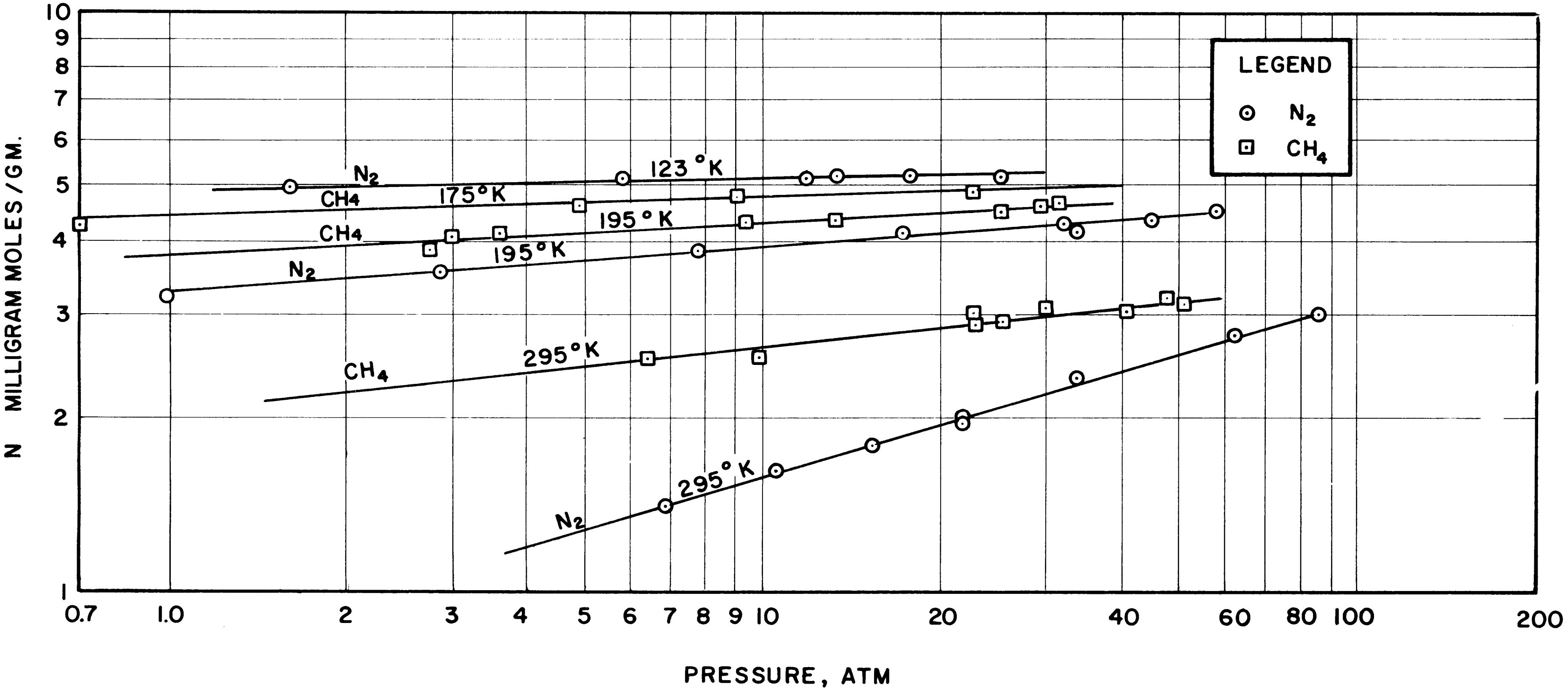


Figure 12. Pure Component Adsorption on 5A Molecular Sieve.

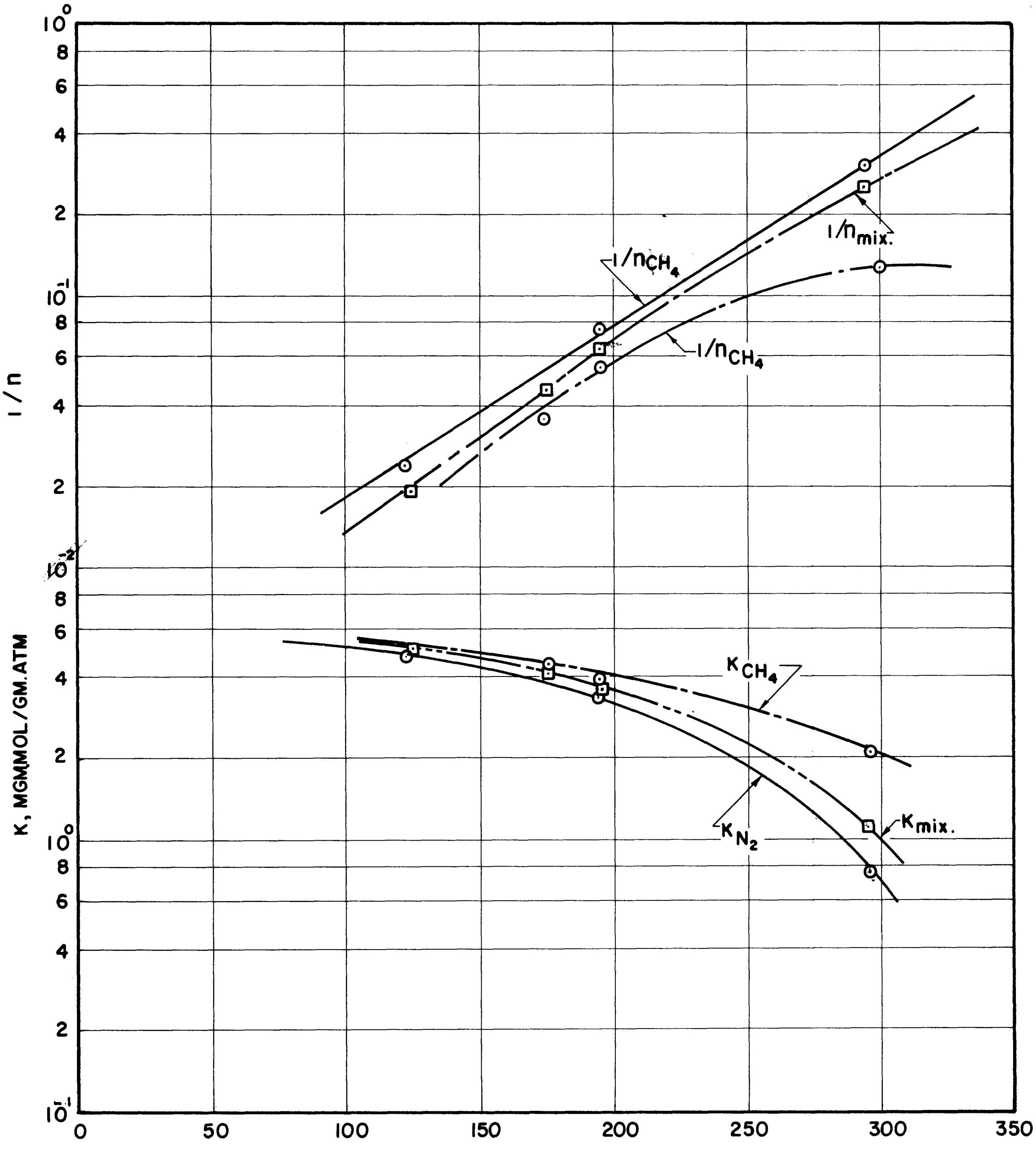


Figure 13. Constants for the Freundlich Equation for Nitrogen and Methane and Their Mixtures (P in ATM.)

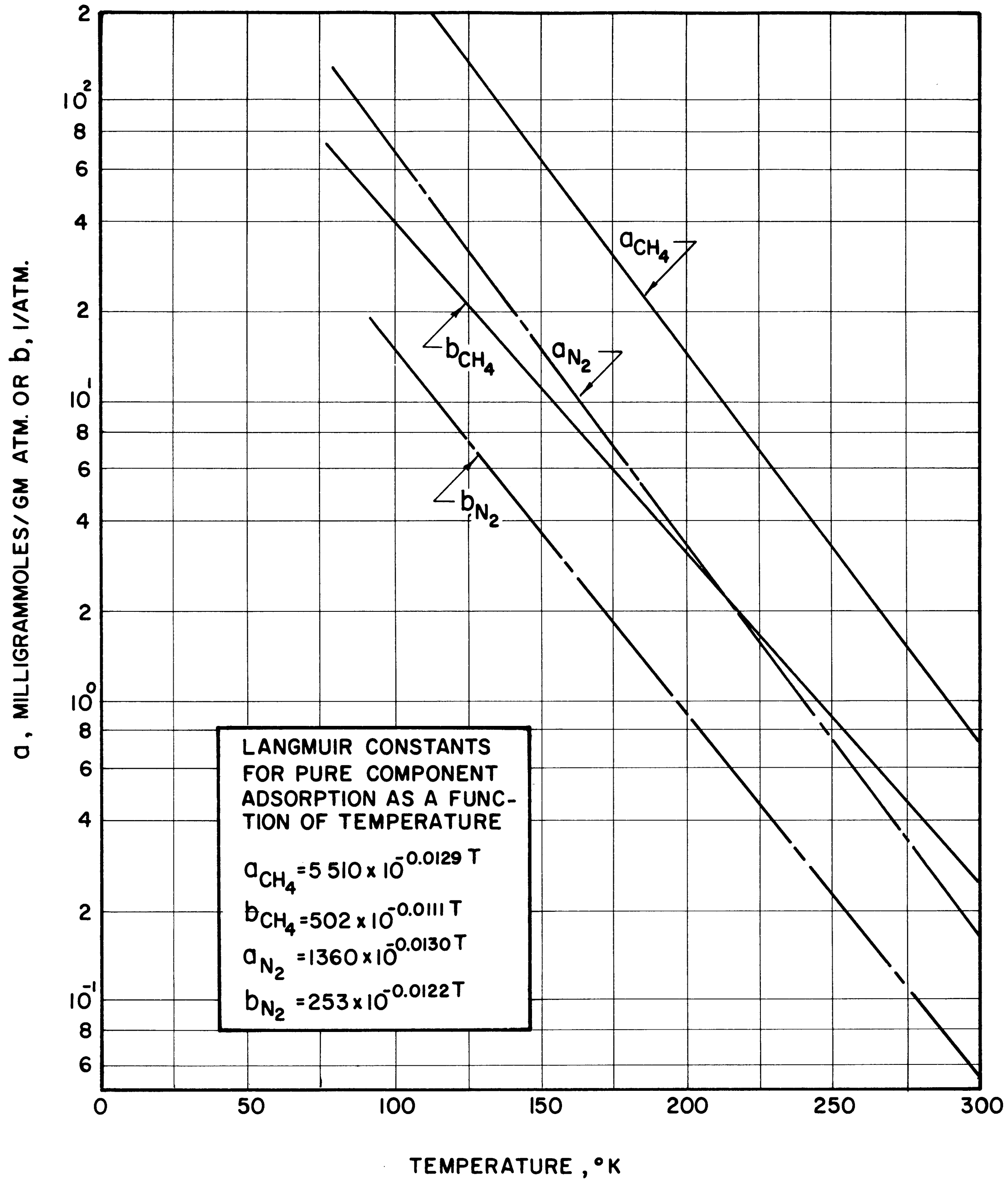


Figure 14. Langmuir Constants for Pure Component Adsorption.

Both relations fit the experimental data rather well with an average correlation coefficient for the logarithmic form of the Freundlich relationship equal to 0.96 for nitrogen and 0.92 for methane. The standard error in the logarithm of the amount adsorbed is less than 0.16 milligram moles per gram (95 per cent confidence) when N is equal to 4 milligram moles per gram. In the case of the Langmuir relationship, the average correlation coefficient is 0.99 plus and a standard error is less than 0.05 which represents a 95 per cent confidence limit of ±0.1 in N, the amount adsorbed.

That both relationships represent the data well is not surprising. Trapnell(60) indicated that, with the proper choice of constants, either the Langmuir or the Freundlich relationship will represent adsorption data in the middle pressure range adequately.

In addition to the Langmuir and Freundlich correlations, two correlations based on the Polanyi Potential Theory were attempted. The first is the one first proposed by Lewis and co-workers(37) where N/ρ_s, the volume adsorbed, is plotted as a function of $T\rho_s \ln f_s/f$, a measure of the adsorption potential. Here, f_s, is the fugacity at the saturation pressure, as determined from an extrapolated Clausius-Clapeyron vapor pressure equation, calculated with the help of the Benedict-Webb-Rubin fugacity relationship. The gas phase fugacity, f, was also evaluated using the B-W-R relationships. The density, ρ_s, which is the important correlating factor, was evaluated at the temperature equal to the temperature of saturation at the equilibrium pressure. The actual density data for methane is due to Bloomer and Parent(10) and for nitrogen is due to Bloomer and Rao.(11)

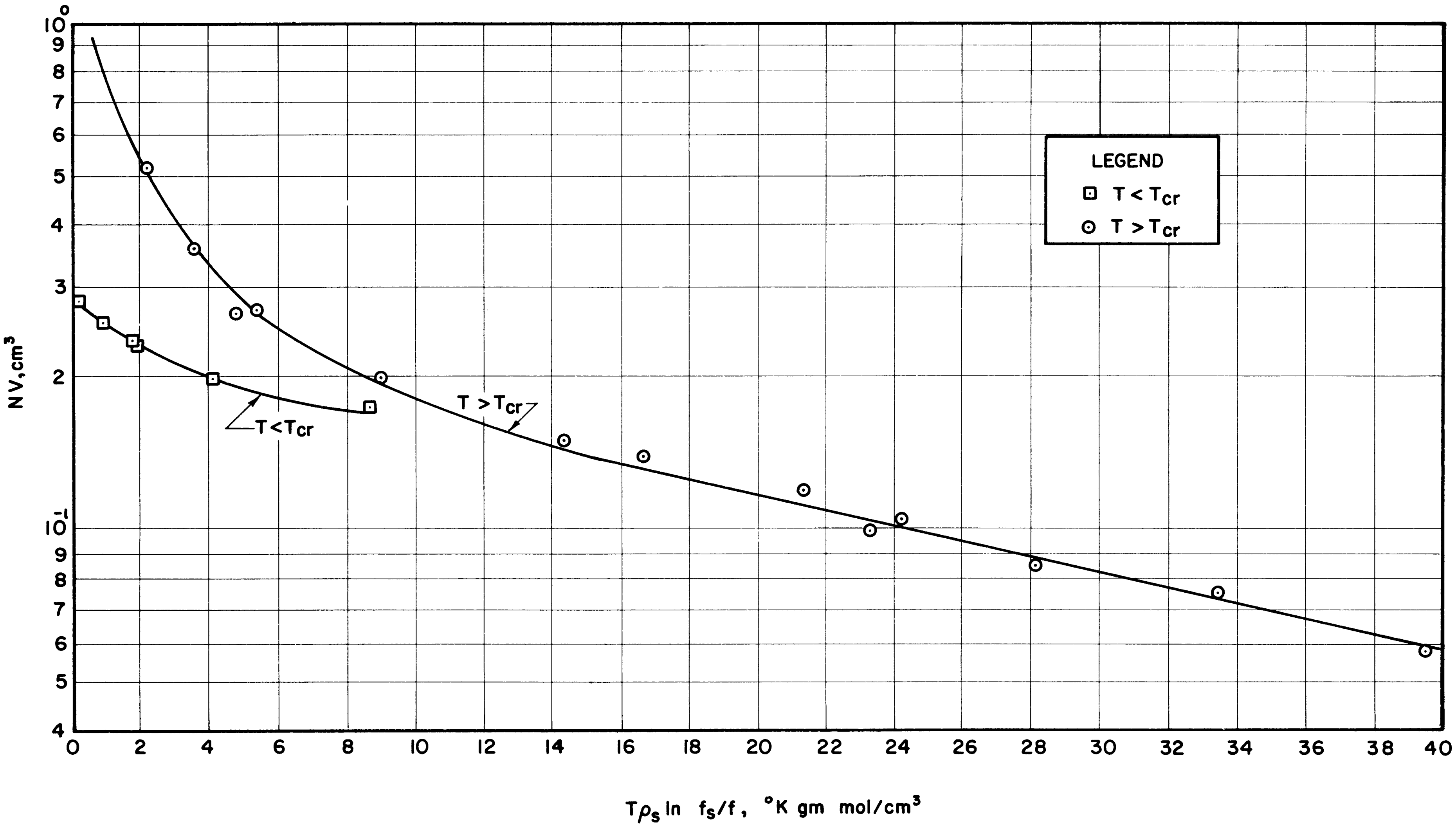


Figure 15. Volume of Nitrogen Adsorbed as a Function of the Adsorption Driving Force.

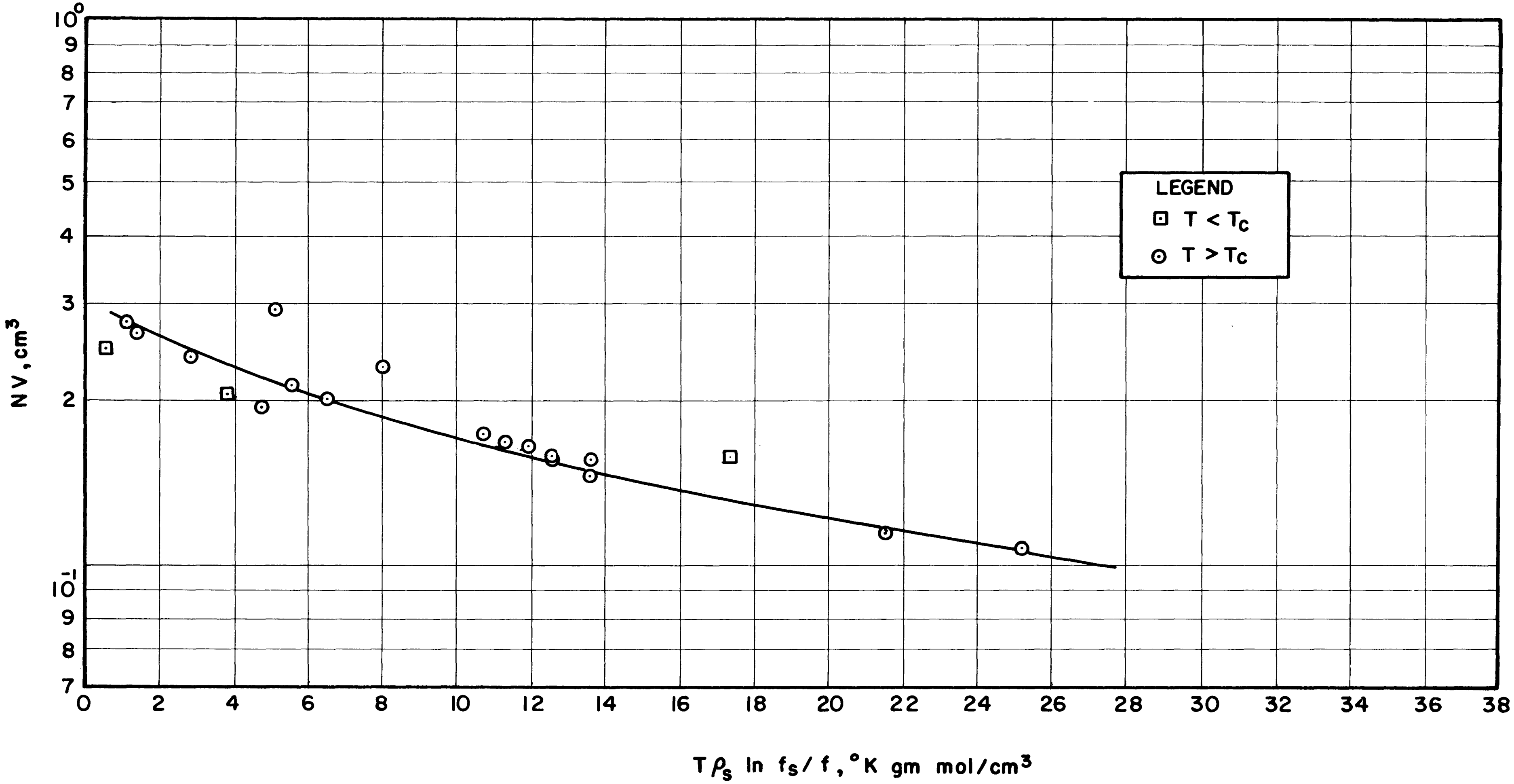


Figure 16. Volume of Methane Adsorbed as a Function of the Adsorption Driving Force.

The correlation for pure nitrogen, as shown in Figure 15, indicates that a good correlation is obtained above the critical point independent of temperature; however, a different correlation appears to exist of adsorption below the critical temperature. This difference could easily be due to an incorrect choice for the density correlating variable. The methane correlation, Figure 16, by this method appears to be quite good for values both above and slightly below the critical with the exception of two points which lie noticeably above the correlating line. These points are obtained from equilibrium data obtained at 40 and 50 atmospheres where the present method of evaluating the adsorbed state density may not predict this density correctly. This same observation can be made about the single point lying well above the nitrogen correlating line.

Correlations for Total Adsorption from a Mixture

A correlation similar to the one detailed in the previous paragraph was attempted for the total amount adsorbed from mixtures of methane and nitrogen. The density in this case was assumed to be the molal average density of the two components in the adsorbed state, using the densities of pure components at their respective saturation temperatures as a basis for obtaining the average. It can readily be seen from Figure 17 that no single correlation could be achieved by this method. The correct choice of density again seems to be the major problem.

The total amount adsorbed from a mixture of nitrogen and methane can also be predicted by either a Freundlich or Langmuir type relationship. The Freundlich equation appears to represent the data better; the necessary constants may be found as a function of temperature in Figure 13. The

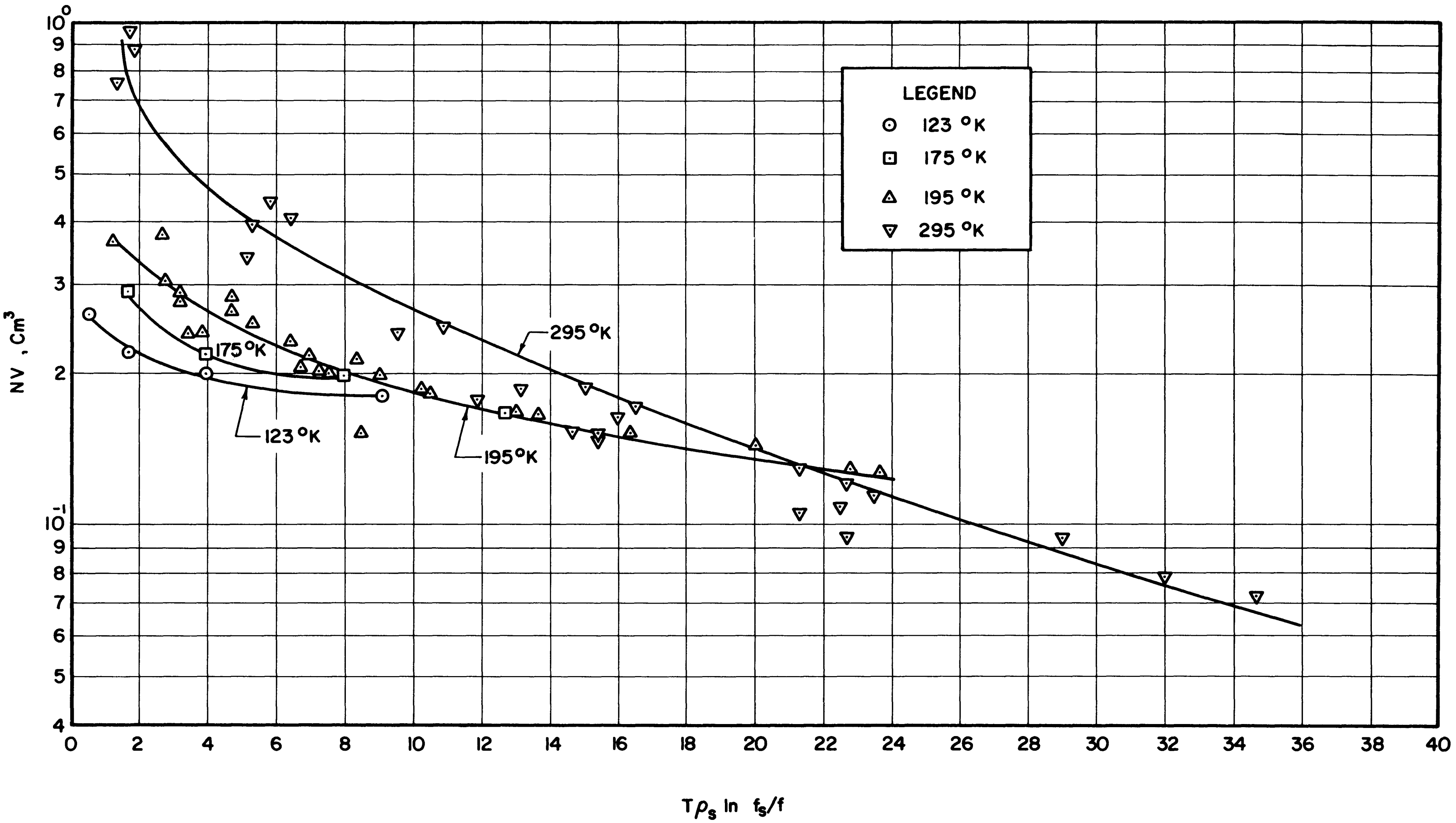


Figure 17. Volume of Nitrogen-Methane Mixtures Adsorbed as a Function of the Adsorption Driving Force.

plots of the total amount adsorbed as a function of pressure and temperature, as found in Figure 11, show that the total adsorption is independent of the composition of the binary gas in equilibrium with the adsorbate. This is not entirely unexpected at the higher temperatures where both gases are well above their critical temperatures. Near the critical point of methane, this behavior is still present and can best be explained by assuming that both gases compete for a given amount of adsorption space which limits the number of molecules adsorbed under a given set of conditions. This assumption would then follow for lower temperatures. More data over a wider range of pressures and compositions at these temperatures would be helpful in confirming this theory.

Another correlating method based on the work of Berényi and Polanyi is that advanced by Dubinin and co-workers. This method has been previously discussed in some detail. Although this method appears to be fundamentally sound, no correlation was possible using Dubinin's methods of evaluating adsorbed phase density as a function of the system temperature, normal boiling point density and van der Waals' density.

Adsorption of Components from a Mixture

Methods for predicting the adsorption of one component from a mixture have not received as much attention as pure component adsorption. The basic work on this area is that of Markham and Benton, which has been previously discussed, and which was examined by Schay. A correlation by these methods proved quite successful. The constants for the equation

$$N_{N_2} = \frac{a'_{N_2} P_{N_2}}{1 + b'_{N_2} P_{N_2} + b''_{CH_4} P_{CH_4}} \tag{23a}$$

and

$$N_{CH_4} = \frac{a'_{CH_4}P_{CH_4}}{1 + b''_{N_2}P_{N_2} + b'_{CH_4}P_{CH_4}} \qquad (23b)$$

are plotted as a function of temperature in Figure 18. It is of some interest that the "a" and "b" constants take on different values from those found in pure component adsorption. This indicates, in conformity with the ideas advanced by Schay, that the adsorbate is not an ideal solution and that certain interactions take place in the adsorbed phase. The constants were obtained using the standard least squares technique and represent the data within plus or minus seven per cent. No simple interaction coefficients, as suggested by Schay were obtained.

A correlation to predict individual component adsorption from a mixture using a Freundlich type relationship

$$\log N_1 = \log K + 1/n_1 \log y_1P + 1/n_2 \log y_1 \qquad (34)$$

was attempted. Although at given temperatures a fair degree of correlation could be obtained, it was not possible to obtain a good correlation of the coefficients as a function of temperature. This may in part be due to the lack of data at intermediate temperatures and a better picture might be obtained with a greater amount of data below the critical temperature. However, the nature of the equation makes it difficult to deduce any fundamental relationship between pure component coefficients and mixed coefficients making it difficult to predict the behavior of the equation constants when mixtures are considered.

From the observation of Lewis and co-workers and the theoretical proof of Schay that

$$\sum \frac{N_i}{N'_i} = 1 \qquad (35)$$

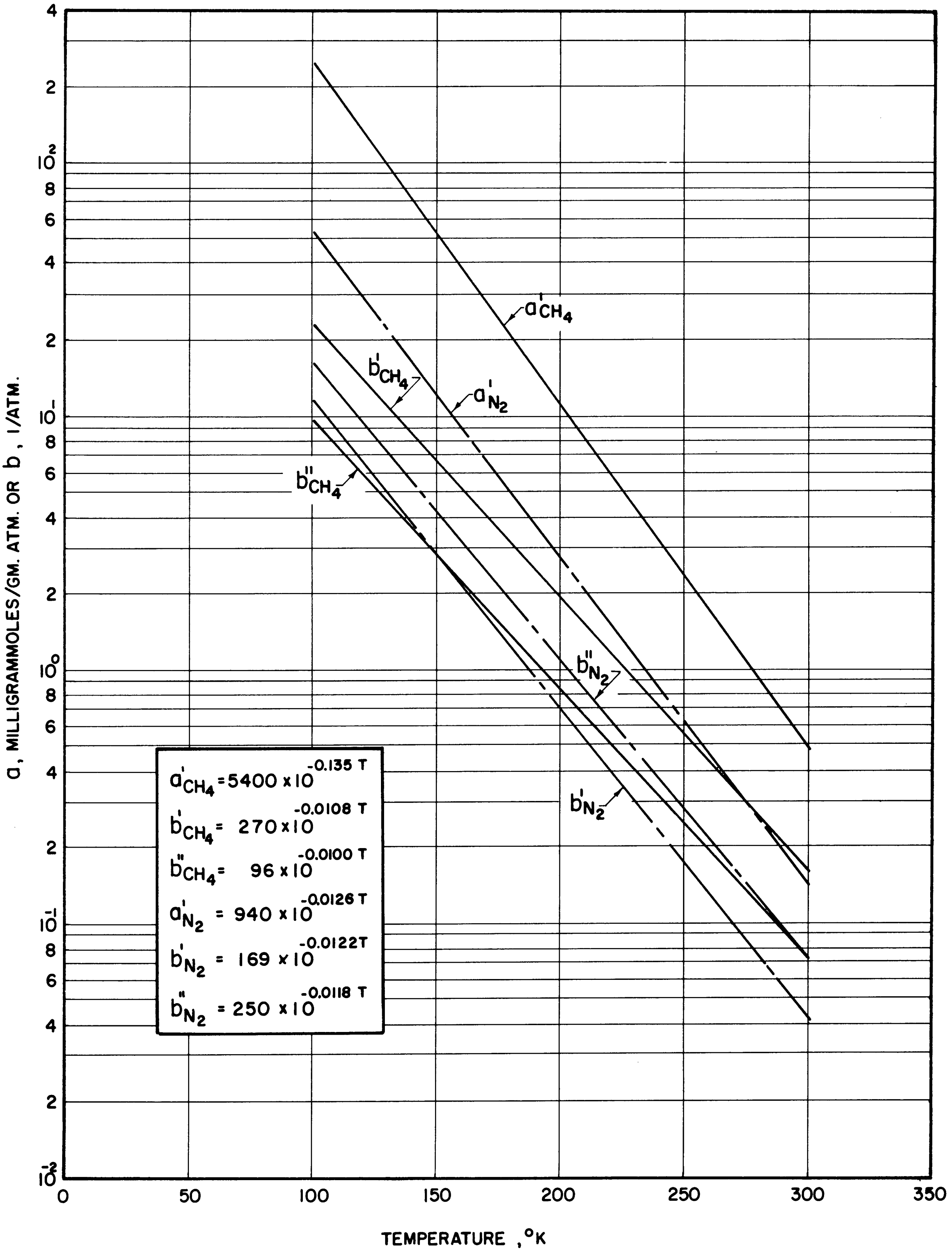


Figure 18. Langmuir Constants for Adsorption From Nitrogen-Methane Mixtures.

for ideal mixtures, a plot of $N_{N_2}/N^{\circ}_{N_2}$ as a function of $N_{CH_4}/N^{\circ}_{CH_4}$ should result in a straight line through the values 0, 1 and 1, 0. If the mixture is non-ideal then the data will lie on one side of the line, which is the case here, as seen in Figure 19.

The relative volatility, as shown in Figure 20, is independent of composition. At the higher pressures above the critical temperature, pressure appears to have little or no effect on the relative volatility. Below the critical point of the mixture, however, as is indicated by the values at 123°K, there is a marked increase in relative volatility with increased pressure. The relative volatility, together with the total loading, will yield the equilibrium loading from a mixture.

Computing Adsorption Loading from the Correlations

It is possible to calculate the amount of each constituent adsorbed from a mixture knowing the temperature, the total pressure and the composition of the equilibrium gas.

As outlined in the sample calculation below, the total amount adsorbed from a mixture can be determined by the Freundlich equation with the appropriate constants, as found in Figure 12. The relative volatility, obtained from Figure 20, is independent of composition over the range of pressures of interest. From the gas phase data and the values of the relative volatility and total loading, the amount of each component may now be computed.

These above calculations may be checked by determining the amount of pure component adsorbed at the system temperature and a pressure equal to its partial pressure in the mixture. These values, together with

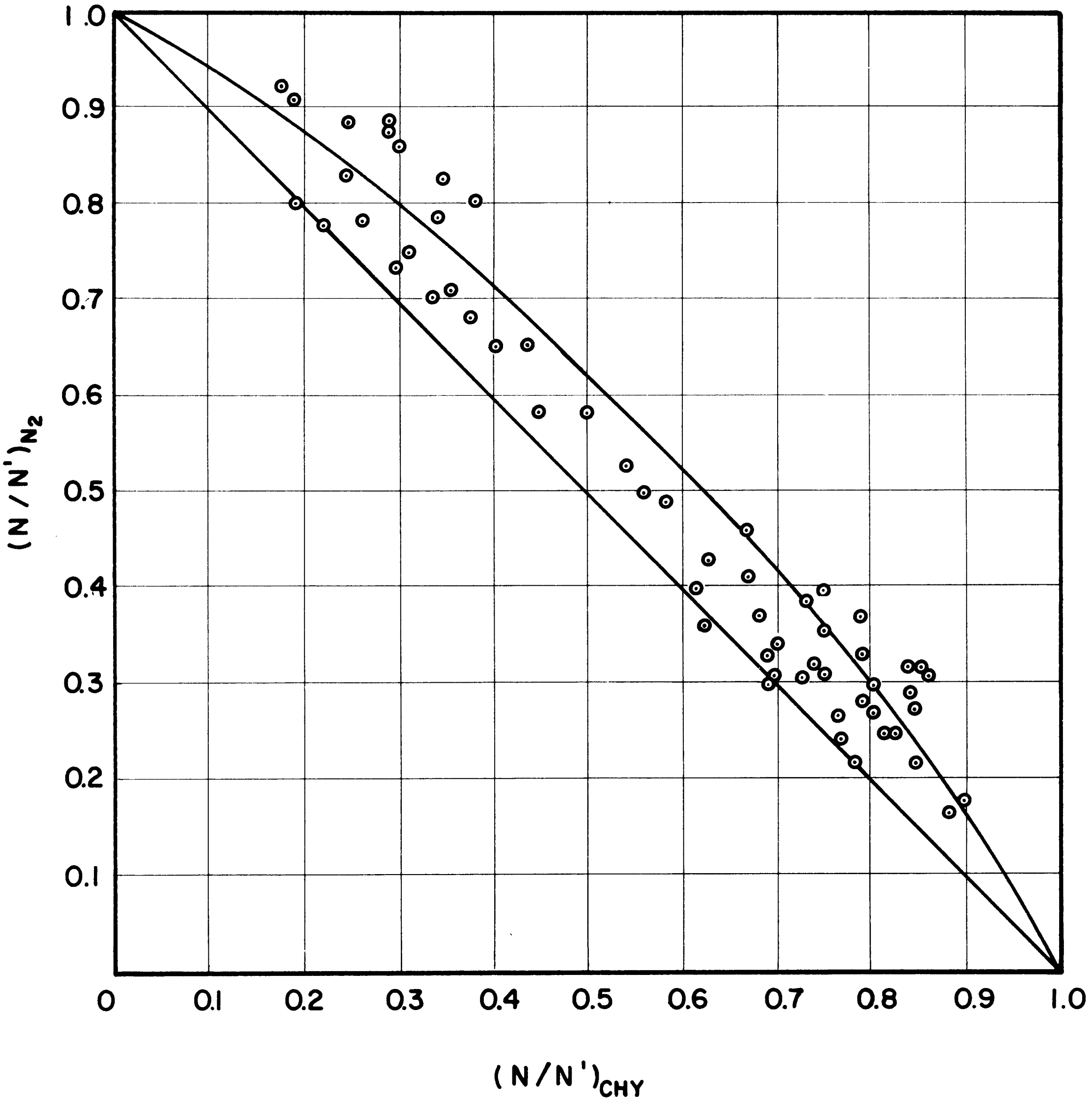


Figure 19. Total Adsorption Correlation on Molecular Sieve 5A.

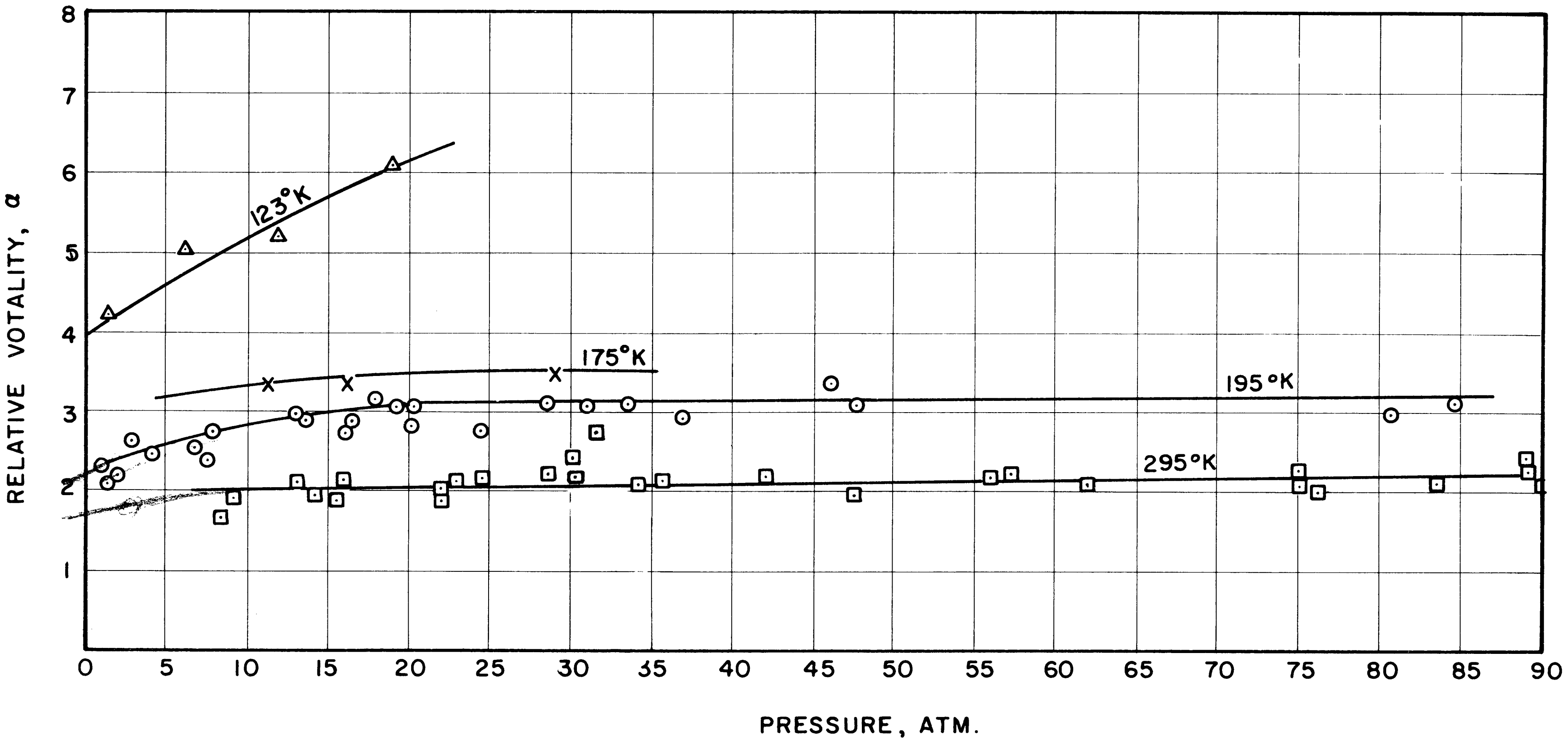


Figure 20. Relative Volatility as a Function of Pressure.
$(\alpha = (y_{N_2}/x_{N_2})/(y_{CH_4}/x_{CH_4}))$.

the amount of component adsorbed, may be used to evaluate the dimensionless factor N/N'. The values of this dimensionless factor for methane and nitrogen should satisfy the restriction placed upon them in Figure 19, a plot of the sum of the values of (N/N') for methane and nitrogen.

The individual component Langmuir equations will also give individual component capacities from a mixture.

Sample Calculation of Binary Adsorption

$P = 15$ atm.

$y_{CH_4} = 0.6$

$P_{CH_4} = 9$ atm.

$P_{N_2} = 6$ atm.

From Figure 20.

$$\alpha = 2.0 = (0.4/X_{N_2})/(0.6/(1-X_{N_2}))$$

then

$$X_{N_2} = 0.25$$

From Figure 11.

$N_T = 2.2$ milligram moles/gm.

then

$N_{N_2} = 2.2 \times 0.25$

$= 0.55$ milligram moles/gm.

and

$N_{CH_4} = 1.65$ milligram moles/gm.

This can now be checked by using Figure 19.

From Figure 12.

$$N_{N_2} = 1.35 \text{ milligram moles/gm at 6 atm.}$$

$$N_{CH_4} = 2.6 \text{ milligram moles/gm at 9 atm.}$$

therefore

$$(N/N')_{N_2} = 0.41$$

$$(N/N')_{CH_4} = 0.64$$

and

$$(N/N')_{N_2} \underline{+ (N/N')_{CH_4} \qquad\qquad}$$

satisfies the relationship illustrated in Figure 12.

The Langmuir relationships predict

$$N_{N_2} = 0.59 \text{ milligram moles/gm.}$$

$$N_{CH_4} = 1.71 \text{ milligram moles/gm.}$$

One or more points were checked at each temperature using both methods and they yielded results that were good to plus or minus ten per cent as indicated by the three examples tabulated below.

TABLE XVII

ACTUAL AND PREDICTED BINARY ADSORPTION

						Predicted			
	Experimental					Relative Volatility Method		Langmuir Equation	
Run	P atm.	T °K	Y_{CH_4}	N_{CH_4} mgm.	N_{N_2} moles/gm.	N_{CH_4}	N_{N_2}	N_{CH_4}	N_{N_2}
16	14.29	295	0.590	1.74	0.62	1.65	0.55	1.71	0.59
64	20.48	195	0.121	1.18	3.05	1.30	3.05	1.31	3.00
81	11.80	123	0.050	1.07	3.96	1.12	3.98	0.72	4.02

At the lowest temperature, 123°K, the Langmuir equation, with the predicted constants, gives low values for the amount of methane adsorbed. Data over a wider range of pressure and composition at this temperature should be evaluated before any definite conclusions regarding these predicted values are made.

An Adsorption Model

Many authors, as discussed previously, have suggested specific models for adsorption as a basis for theoretical development of various correlating equations. It would appear, however, that in light of the present knowledge and development, a modelistic approach based on data in the mid-pressure range is not justified. This is especially true since either the Langmuir or Freundlich relation can be developed from any of a number of models.

The Langmuir equation suggests a mono-layer. In the present studies, the maximum amount adsorbed would cover approximately 95 per cent of the surface area (as measured by the "B E T" method). Many authors, among them Joyner(31) and Brunauer,(14) suggest that a second layer begins to form when the first layer is 35 per cent fulled. In the case of definite porous structures of the type under study here, these assumptions are of little significance. Until a more detailed sub-microscopic study of the adsorption phenomena on sieve type adsorbents can be made, it appears unwise to draw any conclusions as to the method by which the adsorption proceeds.

CONCLUSIONS AND RECOMMENDATIONS

The present study was undertaken to obtain adsorption data for the binary system methane-nitrogen on Molecular Sieves.

For pure component adsorption, both the Langmuir and Freundlich equations will predict the adsorbent loading well, to the saturation pressure below the critical temperature and to about 90 atmospheres above the critical point, over a wide range of temperature. A comparison of the results with limited data previously published by Lewis indicates that the Molecular Sieve has a greater capacity for methane than do either Davison Silica Gel or Columbia G Activated Carbon. Limited data obtained by von Antropff on an activated charcoal indicate that the capacity of the carbon for nitrogen is slightly higher than the capacity of the Molecular Sieve.

A Polanyi type correlation, as those suggested by Dubinin or Lewis and co-workers, would be very useful from a theoretical as well as practical point. Unfortunately, the data did not correlate well using these methods. This appears to be due to the lack of a satisfactory method of predicting the density of the adsorbed state. Therefore, this method of correlation must wait for more fundamental studies than the one attempted here.

For mixtures, for practical purposes, the use of the total loading together with the relative volatility will give sufficiently accurate results. Somewhat more accurate results may be obtained using the individual Langmuir isotherms with proper coefficients as proposed in the section on discussion of results. A study of the constants supports the ideas advanced by Schay regarding interaction of the components in the adsorbed state which changes the values of the isotherm constants from those of the pure component. No simple interaction coefficients as those suggested by Schay could be obtained from a study of the present data. This suggests that more complex models must be assumed or that the interaction is more complex than can be analytically treated at this time.

Much fundamental work remains to be done here before a general method of predicting adsorbate loading from mixtures from pure component adsorption data can be advanced. The present study indicates that there is equal competition for adsorption surface since the total amount adsorbed is independent of the equilibrium gas phase composition. It is quite possible that there is some interference between the molecular species.

This future work must include a better relationship for the phase behavior of mixtures in both the gas and liquid state, a microscopic study of the adsorbate-adsorbent interface, and the phase behavior of the adsorbate in its adsorbed state.

In the present study at low temperatures, the composition range was severely limited as it was difficult to obtain good equilibrium data below one atmosphere due to limitations imposed by the equipment. The study of this system at low pressures and over the whole composition range is recommended.

From the present study it would appear that at the lower temperatures adsorption does not enjoy any advantage as a separative method for nitrogen from methane over vapor-liquid contacting, since the relative volatilities of both methods are about equal and the adsorbent must be regenerated constantly. At higher temperatures, or for final scrubbing of a stream of nitrogen and methane, there may be applications where Molecular Sieve type adsorbents will prove to be quite useful.

APPENDIX A

EXPERIMENTAL DATA

The basic experimental data was converted to absolute pressure and temperature before being used in computations. The mass spectrometer analyses of the samples were reduced to mole fractions. These data, together with the applicable volumes, were then coded on cards which were read by the computer program and served as the basis for computation.

The experimental data as reduced for the computer program may be found in Table XIX. In order to amplify the listing, a sample set of data with the necessary dimensions added may be found in Table XVIII. Each line corresponds to a data card and at the right of the line or card will be found an identification "Run 16". It will be noted that the first line of each series contains only a series of digits on the left. These identify the data set or run to the program as well as the number of samples taken plus desorptions made. The next two data cards or lines of data contain the information regarding the condition of the feed cell before (PI, TI, VI) and after (PF, TF, VF) loading as well as the composition of the gas in the cell ($YI(CH_4)$, $YI(N_2)$). The cards following either refer to samples taken at equilibrium or to desorption. They may easily be distinguished as the equilibrium samples will have a three-digit number (i.e., 002) preceeding the pertinent data, while the desorption data are preceeded by a two digit number preceeded by a minus sign. In addition, no cell pressure (PC) or cell temperature (TC) is recorded for desorption.

The data cards containing equilibrium data, contain the following information in order from left to right:

1) a three digit number identifying the sample,

2) the cell pressure (PC) in psia,

3) the cell temperature (TC) in °K,

4) the pressure of the sample (PS) in psia,

5) the temperature of the sample (TS) in °K,

6) the sample volume (VS) in cc.,

7) the mole fraction methane (YC(CH_4)) in the sample,

8) the mole fraction nitrogen (YC(N_2)) in the sample.

In the data cards which contain desorption information, as previously stated, no cell data will be found. The pressure, temperature and volume of the desorbate, followed by the composition where it was possible to obtain a sample or an assumed value in case no experimental value was available, are recorded.

It will be noted that a number of runs were eliminated from consideration. Several of these were eliminated because the amount desorbed indicated a leak in the system. One run was not used because the liquefaction pressure had been exceeded. In addition, two pure component runs were not used because they did not agree with the remainder of the data as well as the check runs made to check these values.

Runs 116 and 117 were blank runs made to check the adsorptive capacity of the empty cell.

TABLE XVIII

SAMPLE OF EXPERIMENTAL DATA INPUT FOR COMPUTER

Run No.	No. of Data Pts.	
016	004	Run 16

PI	TI	PF	TF	YI_{CH_4}	YI_{N_2}	
415.0 psia	297.0 °K	317.0 psia	297.0 °K	0.7062	0.2938	Run 16

VI	VF	
948.8cc.	959.9cc.	89.72cc.

	PC	TC	PS	TS	VS	YC_{CH_4}	YC_{N_2}	
001	210.0 psia	292.75 °K	29.40 psia	295.2 °K	23.19cc.	0.6612	0.3388	Run 16
002	210.0	292.75	29.4	296.3	23.79	0.5903	0.4097	Run 16
- 03			7.85	294.1	11771.0	1.0	0.0	Run 16
- 04			1.82	293.0	179.6	1.0	0.0	Run 16

TABLE XIX

EXPERIMENTAL DATA

(See Table XVIII for Explanation of Format)

```
013016                                                                                  RUN 13
1845.0          296.0        1615.0       296.0          0.7052       0.2935            RUN 13
  948.8         959.9        89.72
001 1320.0      293.25     147.0     293.3     23.79      0.6240    0.3580              RUN 13
002 1320.0      293.25     147.0     298.0     23.79      0.6362    0.3638              RUN 13
003 1220.0      293.25     147.0     299.6     23.79      0.6396    0.3604              RUN 13
-04                        855.0     299.7     36.89      0.6339    0.3661              RUN 13
005 880.0       295.25     100.0     293.9     23.79      0.6445    0.3555              RUN 13
006 840.0       295.0      45.0      298.7     23.79      0.6360    0.3640              RUN 13
-07                        605.0     298.7     36.89      0.6392    0.3608              RUN 13
008 640.0       295.75     68.0      299.7     23.79      0.6306    0.3694              RUN 13
009 620.0       295.75     12.30     299.7     23.79      0.6412    0.3588              RUN 13
-10                        445.0     298.7     36.89      0.4798    0.5202              RUN 13
011 455.0       292.75     50.7      295.2     23.79      0.6464    0.3536              RUN 13
-12                        325.0     292.25    36.89      0.3780    0.9122              RUN 13
013 190.0       293.25     36.7      296.9     23.79      0.6537    0.3463              RUN 13
-14                        7.91      295.2     11770.0    0.7226    0.2774              RUN 13
-15                        1.86      295.2     11770.0    1.0       0.0                 RUN 13
-16                        16.84     295.2     180.2      1.0       0.0                 RUN 13

014005                                                                                  RUN 14
1550.0          293.75       1340.0       293.75         0.7050       0.2950            RUN 14
  948.8         959.9        89.72
001 1120.0      293.25     112.0     293.0     23.79      0.6387    0.3610              RUN 14
002 1100.0      294.5      117.0     295.4     23.79      0.6330    0.3670              RUN 14
-03                        14.25     294.1     11770.0    0.6700    0.3300              RUN 14
-04                        3.11      293.0     11770.0    0.8377    0.1623              RUN 14
-05                        14.59     295.2     179.6      1.0       0.0                 RUN 14

015005                                                                                  RUN 15
700.0           295.5        575.0        295.5          0.7051       0.2949            RUN 15
  948.8         959.9        89.72
001 420.0       293.25     45.0      297.4     23.79      0.5912    0.4048              RUN 15
002 410.0       293.25     37.0      297.4     23.79      0.5443    0.4556              RUN 15
-03                        8.45      296.3     11774.0    0.6666    0.3334              RUN 15
-04                        2.05      296.3     11770.0    1.0       0.0                 RUN 15
-05                        8.19      296.3     179.6      1.0       0.0                 RUN 15

016004                                                                                  RUN 16
415.0           297.0        317.0        297.0          0.7062       0.2938            RUN 16
  948.8         959.9        89.72
001 210.0       292.75     29.40     295.2     23.79      0.6612    0.3388              RUN 16
002 210.0       292.75     29.4      296.3     23.79      0.5903    0.4097              RUN 16
-03                        7.85      294.1     11771.0    1.0       0.0                 RUN 16
-04                        1.82      293.0     179.6      1.0       0.0                 RUN 16

017011                                                                                  RUN 17
1890.0          295.75       1635.0       296.25         0.2145       0.7855            RUN 17
  948.8         959.9        89.72
001 1335.0      293.25     83.0      296.3     23.79      0.1608    0.8392              RUN 17
002 1335.0      293.25     145.0     297.4     23.79      0.1610    0.8390              RUN 17
-03                        879.0     297.4     36.89      0.1624    0.8376              RUN 17
004 910.0       293.25     100.0     296.3     23.79      0.1610    0.8390              RUN 17
005 880.0       293.5      100.0     296.3     23.79      0.1680    0.8320              RUN 17
-06                        653.0     296.3     36.89      0.2586    0.7414              RUN 17
007 640.0       294.0      71.0      296.3     23.79      0.1661    0.8339              RUN 17
008 620.0       294.0      60.0      296.3     23.79      0.1752    0.8248              RUN 17
-09                        10.34     295.2     11775.0    0.2237    0.7763              RUN 17
-10                        1.7       296.3     11775.0    1.0       0.0                 RUN 17
-11                        1.62      295.2     179.6      1.0       0.0                 RUN 17

018006                                                                                  RUN 18
1140.0          297.0        970.0        297.0          0.2160       0.7840            RUN 18
  948.8         959.9        89.72
001 695.0       296.25     79.0      298.6     23.79      0.1548    0.8452              RUN 18
002 670.0       296.25     65.0      298.6     23.79      0.1526    0.8473              RUN 18
003 660.0       294.25     76.0      298.6     23.79      0.1595    0.8404              RUN 18
-04                        10.79     295.2     11775.0    0.1995    0.8005              RUN 18
-05                        1.6       295.2     11770.0    1.0       0.0                 RUN 18
-06                        3.74      295.2     179.6      1.0       0.0                 RUN 18

019004                                                                                  RUN 19
570.0           296.0        467.0        296.0          0.2218       0.7782            RUN 19
  948.8         959.9        89.72
001 335.0       294.25     36.0      300.2     23.79      0.1459    0.8541              RUN 19
002 335.0       294.25     35.0      300.2     23.79      0.1459    0.8541              RUN 19
003 335.0       295.25     35.0      299.7     23.79      0.1456    0.8544              RUN 19
-04                        8.005     296.3     11776.0    0.1983-   0.8016              RUN 19

020005                                                                                  RUN 20
01530.0         0295.5       01325.0      0295.75        0.7722       0.2278            RUN 20
  948.8         959.9        89.72
001 01100.0     296.0      127.0     300.8     23.79      0.7051    0.2948              RUN 20
002 1075.0      296.0      125.0     300.8     23.79      0.7038    0.2962              RUN 20
-03                        13.42     298.0     11777.8    0.7473    0.2527              RUN 20
-04                        1.96      296.4     11769.7    1.0       0.0                 RUN 20
-05                        0.11      296.4     179.7      1.0       0.0                 RUN 20

021005                                                                                  RUN 21
01300.0         298.0        1128.0       298.0          0.7715       0.2285            RUN 21
  948.8         959.9        89.72
001 845.0       295.5      98.0      297.5     23.79      0.6983    0.3016              RUN 21
002 825.0       293.5      83.0      297.5     23.79      0.7003    0.2997              RUN 21
-03                        13.323    295.8     11776.7    0.7405    0.2594              RUN 21
-04                        1.742     296.3     11769.8    1.0       0.0                 RUN 21
-05                        0.319     296.3     179.7      1.0       0.0                 RUN 21
```

```
022005                                                                    RUN 22
857.0       296.5      722.0        296.5      0.7631       0.2369        RUN 22
  948.8      959.9     89.72
001500.0    293.75   25.0     296.9     49.59     0.6747   0.3253         RUN 22
002500.0    294.25   55.0     299.1     23.79     0.6627   0.3373         RUN 22
-03                  10.461   297.4     11775.1   0.7329   0.2671         RUN 22
-04                  1.431    296.6     11769.8   1.0      0.0            RUN 22
-05                  0.561    297.0     179.7     1.0      0.0            RUN 22

023004                                                                    RUN 23
705.0       295.5       595.0       295.5      0.7679       0.2321        RUN 23
  948.8      959.9     89.72
001 400.0   293.75   45.0     298.6     23.79     0.6675   0.3325         RUN 23
002 360.0   293.75   45.0     298.6     23.79     0.6670   0.3330         RUN 23
-03                  9.34     296.3     11774.6   0.7335   0.2665         RUN 23
-04                  1.189    296.3     11769.9   1.0      0.0            RUN 23

024005                                                                    RUN 24
425.0       298.25     337.0        298.25     0.7671       0.2329        RUN 24
  948.8      959.9     89.72
001 235.0   296.5    21.7     300.7     23.79     0.6512   0.3488         RUN 24
002 225.0   296.5    20.7     300.7     23.79     0.6561   0.3439         RUN 24
-03                  7.135    298.6     11773.4   0.7280   0.2720         RUN 24
-04                  0.880    298.6     11769.0   1.0      0.0            RUN 24
-05                  0.348    300.0     179.7     1.0      0.0            RUN 24

025003                                                                    RUN 25
1130.0      299.0      975.0        299.5      0.9895       0.0105        RUN 25
  948.8      959.9     89.72
001 700.0   293.25   4.05     296.3     11772.2   0.9830   0.0170         RUN 25
002 330.0   293.25   36.7     300.7     23.79     0.9891   0.0109         RUN 25
-03                  10.036   298.6     11771.2   1.0      0.0            RUN 25

026002                                                                    RUN 26
917.0       298.5      775.0        298.5      0.9952       0.0047        RUN 26
  948.8      959.9     89.72
001 590.0   297.5                               1.0      0.0            RUN 26
-02                  13.13    299.7     11771.6   1.0      0.0            RUN 26


027003                                                                    RUN 27
770.0       297.75     640.0        297.75     1.0          0.0           RUN 27
  948.8      959.9     89.72
001 440.0   296.25                              1.0      0.0            RUN 27
002 450.0   296.0                               1.0      0.0            RUN 27
-03                  11.776   298.6     11771.2   1.0      0.0            RUN 27

028004                                                                    RUN 28
600.0       297.0      477.0        297.0      1.0          0.0           RUN 28
  948.8      959.9     89.72
001 380.0   298.25                              1.0      0.0            RUN 28
002 380.0   296.25                              1.0      0.0            RUN 28
003 380.0   295.75                              1.0      0.0            RUN 28
-04                  10.887   299.1     11771     1.0      0.0            RUN 28

029005                                                                    RUN 29
1895.0      297.75     1630.0       298.0      0.0013       0.9985        RUN 29
  948.8      959.9     89.72
001 1255.0  293.25                              0.0      1.0            RUN 29
002 1270.0  294.75                              0.0      1.0            RUN 29
-03                  915.0    299.7     36.89     0.0      1.0            RUN 29
004 910.0   295.0                               0.0      1.0            RUN 29
-05                  14.738   296.9     11772.0   0.0      1.0            RUN 29

029005                                                                    RUN 29A
1890.0      297.75     1632.0       298.0      0.0          1.0           RUN 29A
  948.8      959.9     89.72
001 1255.0  293.25                              0.0      1.0            RUN 29A
002 1270.0  294.75                              0.0      1.0            RUN 29A
-03                  3.1519   298.      11771.2   0.0      1.0            RUN 29A
004 910.0   295.0                               0.0      1.0            RUN 29A
-05                  14.738   296.9     11772.0   0.0      1.0            RUN 29A

030005                                                                    RUN 30
1380.0      298.5      1180.0       298.5      0.0          1.0           RUN 30
  948.8      959.9      89.72
001 925.0   295.5                               0.0      1.0            RUN 30
002 925.0   296.25                              0.0      1.0            RUN 30
003 940.0   296.25                              0.0      1.0            RUN 30
004 940     296.25                              0.0      1.0            RUN 30
-05                  14.835   297.0     11770.4   0.0      1.0            RUN 30
```

```
031004                                                                RUN 31
758.0         295.75      627.0         295.75      0.0        1.0    RUN 31
  948.8        959.9        89.72
001 505.0     299.5                                 0.0      1.0      RUN 31
002 490.0     293.75                                0.0      1.0      RUN 31
003 495.0     295.25                                0.0      1.0      RUN 31
-04                     10.442    295.8    11771.0  0.0      0.0      RUN 31

032002
  500.0       295.2       402.0         295.2        0.0        1.0   RUN 32
  948.8        959.9        89.72
001 317.0     295.5                                 0.0      1.0      RUN 32
-02                     7.87      296.9    11770.8  0.0      1.0      RUN 32

033002                                                                RUN 33
397.0          296.2       312.0         296.25      0.0        1.0   RUN 33
948.8         959.9       89.7                                        RUN 33
001 230.0     296.0     10.0      297.6    0.0      0.0      1.0      RUN 33
-02                     6.64      297.6    11769.9  0.0      1.0      RUN 33

034014                                                                RUN 34
1705.00       300.5       1310.0        300.5       0.2291     0.7709 RUN 34
  948.8       959.9         89.72
001 1235.0    194.75    160.0     305.2    23.79    0.1503   0.8497   RUN 34
002 1200.0    194.75    157.0     305.2    23.79    0.1530   0.8470   RUN 34
-03                     880.0     305.2    36.89    0.2318   0.7682   RUN 34
004 1070.0    197.5     127.0     302.4    23.79    0.1464   0.8536   RUN 34
-05                     14.10     301.9    11777.1  0.1478   0.8522   RUN 34
-06                     3.71      301.9    11771.6  0.2832   0.7168   RUN 34
-07                     2.01      301.9    11770.2  1.0      0.0      RUN 34
-08                     1.02      301.9    11769.6  1.0      0.0      RUN 34
-09                     0.657     300.8    11769.4  1.0      0.0      RUN 34
-10                     0.425     300.8    11769.2  1.0      0.0      RUN 34
-11                     0.193     300.8    11769.0  1.0      0.0      RUN 34
-12                     0.097     300.8    11769.0  1.0      0.0      RUN 34
-13                     0.116     300.8    11769.0  1.0      0.0      RUN 34
-14                     0.029     300.8    11769.0  1.0      0.0      RUN 34

035005                                                                RUN 35
1002.0         300.75     733.00         300.75     0.2299     0.7701 RUN 35
  948.8        959.9        89.72
001 685.0     194.75    88.0      299.1    23.79    0.1205   0.8795   RUN 35
002 670.0     194.75    86.0      299.1    23.79    0.1149   0.8851   RUN 35
-03                     10.364    296.3    11775.0  0.1276   0.8724   RUN 35
-04                     2.456     296.3    11770.8  1.0      0.0      RUN 35
-05                     4.734     296.5    1176-.0  1.0      0.0      RUN 35


036009                                                                RUN 36
760.0         305.0       538.0         305.0       0.2302     0.7618 RUN 36
  948.8        959.9        89.72
001 425.0     191.33    50.0      306.3    23.79    0.1101   0.8899   RUN 36
002 412.0     191.33    50.0      306.3    23.79    0.1137   0.8863   RUN 36
-03                     7.909     303.0    11773.8  0.1230   0.8770   RUN 36
-04                     3.171     296.9    11771.2  1.0      0.0      RUN 36
-05                     2.688     301.9    11771.0  1.0      0.0      RUN 36
-06                     0.812     301.9    11770.0  1.0      0.0      RUN 36
-07                     0.348     302.4    11770.0  1.0      0.0      RUN 36
-08                     0.048     302.4    11770.0  1.0      0.0      RUN 36
-09                     0.006     303.0    11770.0  1.0      0.0      RUN 36

037006                                                                RUN 37
568.0         309.75      383.0              309.75 0.2480     0.7520 RUN 37
  948.8        959.9        89.72
001 242.0     193.67    25.0      303.5    23.79    0.1182   0.8818   RUN 37
002 240.0     193.67    25.0      303.5    23.79    0.1124   0.8876   RUN 37
-03                     5.105     301.9    11772.3  0.1150   0.8850   RUN 37
-04                     5.443     305.2    11772.6  0.2284   0.7716   RUN 37
-05                     1.682     304.1    11770.5  1.0      0.0      RUN 37
-06                     0.288     303.0    1176-.4  1.0      0.0      RUN 37

039006                                                                RUN39
970.00         302.7      703.0         302.7      0.7159      0.2841
  948.8        959.9        89.72
001 700.0     192.45    89.0      301.0    23.79    0.6058   0.3942   RUN39
-02                     10.055    298.8    11774.9  0.5996   0.4004   RUN39
-03                     3.016     297.1    11771.2  0.7094   0.2906   RUN39
-04                     4.467     299.9    11772.0  0.8382   0.1618   RUN39
-05                     2.204     299.9    11770.8  0.9175   0.0824   RUN39
-06                     0.197     299.9    11770.0  1.0      0.0      RUN39

040004                                                                RUN40
727.0         303.95      520.0         303.95      0.7256     0.2744 RUN 40
  948.8        959.9        89.72
001 420.0     192.2     51.0      298.8    23.79    0.5558   0.4442   RUN40
-02                     6.932     296.5    11773.2  0.5635   0.4365   RUN40
-03                     7.986     296.5    11773.8  0.7896   0.2104   RUN40
-04                     1.241     297.6    11770.0  1.0      0.0      RUN40

041007                                                                RUN41
512.0         305.2       370.0         305.2       0.7101     0.2899 RUN41
  948.8        959.9        89.72
001 167.0     191.9     20.0      302.1    23.79    0.5030   0.4970   RUN41
002 167.0     191.9     20.0      302.1    23.79    0.5010   0.4990   RUN41
-03                     4.215     298.8    11772.0  0.5380   0.4620   RUN41
-04                     4.796     298.8    11772.1  0.7292   0.2708   RUN41
-05                     2.651     301.0    11771.1  1.0      0.0      RUN41
-06                     0.657     301.0    11770.0  1.0      0.0      RUN41
-07                     0.135     301.0    11770.0  1.0      0.0      RUN41
```

```
042003                                                                   RUN42
1810.0      305.7      1398.0      305.7      0.5093      0.4907         RUN42
  948.8      959.9      89.72
001 580.0   194.45   79.0      296.5     23.79     0.4370   0.5629       RUN42
002 565.0   194.45   77.0      296.5     23.79     0.4369   0.5531       RUN42
-03                  16.881    297.6     11774.7   0.4427   0.5573       RUN42

043005                                                                   RUN43
1295.0      301.25     1055.0      301.25     0.5759      0.4241         RUN43
  948.8      959.9      89.72
001 550.0   191.9    72.0      297.1     23.79     0.4048   0.5952       RUN43
002 540.0   191.9    70.0      297.1     23.79     0.4054   0.5946       RUN43
-03                  9.668     298.2     11774.3   0.4176   0.5824       RUN43
-04                  7.696     298.8     11773.2   0.7011   0.2989       RUN43
-05                  1.025     297.6     11770.8   1.0      0.0          RUN43

044004                                                                   RUN44
948.00      302.75     772.0       302.75     0.6360      0.3640         RUN44
  948.8      959.9      89.72
001 240.0   194.45   22.0      299.9     23.79     0.4059   0.5941       RUN44
-02                  7.429     296.0     11772.8   0.4866   0.5134       RUN44
-03                  5.279     296.0     11772.0   0.7479   0.2521       RUN44
-04                  0.812     295.4     11769.6   1.0      0.0          RUN44

045006                                                                   RUN45
1867.0      301.5      1455.0      301.5      0.5499      0.4511         RUN45
  948.8      959.9      89.72
001  1130.0 192.5    160.0     297.1     23.79     0.4764   0.5236       RUN45
-02                  19.530    296.5     11779.6   0.4494   0.5506       RUN45
-03                  8.160     296.5     11773.6   0.6571   0.3429       RUN45
-04                  2.340     296.5     11770.5   0.75     0.25         RUN45
-05                  0.367     297.6     11770.0   1.0      0.0          RUN45
-06                  0.048     297.6     11770.0   1.0      0.0          RUN45

046005                                                                   RUN46
915.0       302.75     673.0       298.25     0.5466      0.4534         RUN46
  948.8      959.9      89.72
001 540.0   194.95   70.0      295.4     23.79     0.3887   0.6113       RUN46
-02                  9.630     296.5     11774.3   0.3954   0.6046       RUN46
-03                  6.652     296.5     11772.7   0.6537   0.3463       RUN46
-04                  2.224     296.5     11770.0   0.75     0.25         RUN46
-05                  0.155     296.5     11769.0   1.0      0.0          RUN46

048005                                                                   RUN48
577.0       298.25     402.0       298.25     0.6522      0.3478         RUN48
  948.8      959.9      89.72
001 267.0   192.5    35.0      298.8     23.79     0.4512   0.5488       RUN48
-02                  10.538    299.9     11774.8   0.5479   0.4521       RUN48
-03                  4.041     299.3     11771.3   0.8133   0.1869       RUN48
-04                  1.006     299.9     11769.7   1.0      0.0          RUN48
-05                  0.048     299.9     11769.0   1.0      0.0          RUN48

049005                                                                   RUN49
1593.0      298.75     1240.0      298.75     0.0007      0.9993         RUN49
  948.8      959.9      89.72
001  1145.0 192.9    67.0      298.8     49.6      0.0007   0.9993       RUN49
-02                  15.237    301.5     11777.2   0.0009   0.9991       RUN49
-03                  9.978     299.9     11774.4   0.0018   0.9982       RUN49
-04                  0.309     299.9     11769.3   0.0      1.0          RUN49
-05                  0.010     299.9     11769.0   0.0      1.0          RUN49

050004                                                                   RUN50
1213.0      305.0      940.0       305.0      0.0006      0.9994         RUN50
  948.8      959.9      89.72
001 850.0   193.9    99.0      300.9     23.79     0.0016   0.9984       RUN50
-02                  15.798    299.9     11779.6   0.0013   0.9987       RUN50
-03                  4.738     300.4     11771.8   0.0      1.0          RUN50
-04                  0.512     299.9     11769.5   0.0      1.0          RUN50

051003                                                                   RUN51
825.0       298.0      600.0       298.0      0.0009      0.9991         RUN51
  948.8      959.9      89.72
001 470.0   194.7    12.820    299.3     11775.9   0.0009   0.9991       RUN51
-02                  4.670     298.8     11771.6   0.0      1.0          RUN51
-03                  0.058     298.8     11769.0   0.0      1.0          RUN51

052004                                                                   RUN52
750.4       298.2      541.9       298.2      0.9920      0.0080         RUN52
 961.1      972.2       89.72
001 436.4   195.9    60.0      302.0     23.79     0.9897   0.0103       RUN52
-02                  7.677     299.8     11783.0   0.9842   0.0158       RUN52
-03                  10.364    298.7     11758.7   0.9940   0.0060       RUN52
-04                  0.590     298.7     11733.5   1.0      0.0          RUN52

053004                                                                   RUN53
508.0       298.6      345.0       298.6      0.9900      0.0100         RUN53
 961.1      972.2       89.72
001 133.46  195.6    20.0      301.5     23.79     0.9860   0.0140       RUN53
-02                  4.892     299.8     11786.1   0.9884   0.0116       RUN53
-03                  9.127     300.4     11758.0   1.0      0.0          RUN53
-04                  0.300     300.9     11753.0   1.0      0.0          RUN53

056005                                                                   RUN56
687.0       296.9      493.5       296.9      0.9904      0.0096         RUN56
 961.1      972.2       89.72
001 365.0   193.8    47.0      299.3     23.79     0.9883   0.0118       RUN56
-02                  6.710     299.3     11782.5   0.9862   0.0138       RUN56
-03                  10.055    299.3     11783.0   1.0      0.0          RUN56
-04                  1.006     299.8     11779.0   1.0      0.0          RUN56
-05                  0.029     299.8     11779.0   1.0      0.0          RUN56
```

```
057004                                                                    RUN57
470.0       297.4      333.0        297.4       0.9887      0.0113       RUN57
 961.1      972.2       89.72
001  52.0   195.5    20.0      299.8      23.79     0.9814    0.0186      RUN57
-02                  11.254    299.8      11784.9   0.9919    0.0081      RUN57
-03                  0.986     298.7      11779.0   1.0       0.0         RUN57
-04                  0.029     298.7      11779.0   1.0       0.0         RUN57

058006                                                                    RUN58
299.0       296.2      172.8        296.2       0.9895      0.0105       RUN58
 961.1      972.2       89.72
-01                  337.3     296.2      -972.2    0.9914    0.0086      RUN58
-02                  296.9     296.2      972.2     0.9914    0.0086      RUN58
003 193.0   195.0    25.0      300.4      23.79     0.9849    0.0151      RUN58
-04                  11.873    298.7      11780.0   0.9894    0.0106      RUN58
-05                  2.881     299.3      11780.0   1.0       0.0         RUN58
-06                  0.211     299.3      11780.0   1.0       0.0         RUN58

059003                                                                    RUN59
236.4       298.4      102.2        298.4       0.9797      0.0203       RUN59
 961.1      972.2       89.72
001 40.0    194.9    40.0      300.9      23.79     0.9830    0.0170      RUN59
-02                  10.287    300.4      11780.0   0.9918    0.0082      RUN59
-03                  0.850     300.4      11780.0   1.0       0.0         RUN59

060005                                                                    RUN60
770.5       298.16     556.0        798.16      0.5241      0.4759       RUN60
 961.1      972.2       89.72
001 485.0   195.8    60.0      298.2      23.79     0.3517    0.6483      RUN60
-02                  7.793     299.3      11780.0   0.3572    0.6428      RUN60
-03                  9.108     299.8      11780.0   0.500     0.500       RUN60
-04                  1.122     299.3      11780.0   1.0       0.0         RUN60
-05                  0.072     299.3      11780.0   1.0       0.0         RUN60

060004                                                                    RUN60A
537.9       295.8      369.6        296.2       0.5205      0.4795       RUN60A
 961.1      972.2       89.72
001 178.0   194.4    20.0      298.7      23.79     0.5066    0.4934      RUN60A
-02                  13.014    299.8      11780.0   0.3060    0.6940      RUN60A
-03                  0.870     299.8      11780.0   1.0       0.0         RUN60A
-04                  0.012     299.8      11780.0   1.0       0.0         RUN60A

061004                                                                    RUN61
349.4       296.9      203.1        296.9       0.5208      0.4792       RUN61
 961.1      972.2       89.72
001 95.6    195.5    13.26     297.0      23.79     0.3139    0.6861      RUN61
-02                  10.887    293.2      11780.0   0.4959    0.5041      RUN61
-03                  1.305     297.6      11780.0   0.500     0.500       RUN61
-04                  0.064     297.6      11780.0   1.0       0.0         RUN61

062004                                                                    RUN62
193.0       296.2      66.8         296.2       0.5195      0.4805       RUN62
 961.1      972.2       89.72
001 29.0    192.8    24.0      295.4      23.79     0.3344    0.6656      RUN62
-02                  9.707     299.8      11780.0   0.5065    0.4935      RUN62
-03                  0.831     299.3      11780.0   1.0       0.0         RUN62
-04                  0.041     299.3      11780.0   1.0       0.0         RUN62

063005                                                                    RUN63
381.2       296.2      559.0        296.2       0.2411      0.7589       RUN63
 961.1      972.2       89.72
001 550.0   200.9    65.0      295.4      23.79     0.1382    0.8618      RUN63
-02                  8.373     297.6      11780.0   0.1382    0.8618      RUN63
-03                  8.412     298.7      11780.0   0.3078    0.6922      RUN63
-04                  0.928     298.7      11780.0   1.0       0.0         RUN63
-05                  0.039     298.7      11780.0   1.0       0.0         RUN63

064005                                                                    RUN64
533.8       296.2      349.4        296.4       0.2405      0.7595       RUN64
 961.1      972.2       89.72
001 301.0   192.8    37.0      294.3      23.79     0.1214    0.8786      RUN64
-02                  12.105    298.7      11780.0   0.1962    0.8038      RUN64
-03                  2.630     298.7      11780.0   0.500     0.500       RUN64
-04                  0.261     298.7      11780.0   1.0       0.0         RUN64
-05                  0.014     298.7      11780.0   1.0       0.0         RUN64

065005                                                                    RUN65
336.2       296.9      186.0        296.9       0.2402      0.7598       RUN65
 961.1      972.2       89.72
001 111.5   192.8    14.7      296.5      23.79     0.1261    0.8739      RUN65
002 106.0   192.8    14.7      296.5      23.79     0.1263    0.8737      RUN65
-03                  11.505    299.8      11780.0   0.2274    0.7726      RUN65
-04                  0.870     298.7      11780.0   0.500     0.500       RUN65
-05                  0.021     299.8      11780.0   1.0       0.0         RUN65

066004                                                                    RUN66
177.9       298.66     61.8         298.66      0.2395      0.7605       RUN66
 961.1      972.2       89.72
001 20.3    190.5    8.35      298.2      23.79     0.1326    0.8674      RUN66
-02                  8.798     301.5      11780.0   0.2282    0.7718      RUN66
-03                  0.657     301.5      11780.0   0.500     0.500       RUN66
-04                  0.029     301.5      11780.0   1.0       0.0         RUN66

067005                                                                    RUN67
755.4       297.91     535.8        297.91      0.7100      0.2900       RUN67
 961.1      972.2       89.72
001 458.5   193.83   60.0      294.3      23.79     0.5638    0.4362      RUN67
-02                  8.257     299.8      11780.0   0.5740    0.4260      RUN67
-03                  9.475     298.7      11780.0   0.8185    0.1815      RUN67
-04                  0.503     298.7      11780.0   1.0       0.0         RUN67
-05                  0.029     298.7      11780.0   1.0       0.0         RUN67

068005                                                                    RUN68
515.7       298.16     323.2        298.16      0.7122      0.2878       RUN68
 961.1      972.2       89.72
001 241.0   192.84   28.0      296.5      23.79     0.5312    0.4688      RUN68
-02                  12.086    299.8      11780.0   0.6803    0.3196      RUN68
-03                  2.765     299.8      11780.0   0.7500    0.2500      RUN68
-04                  0.193     299.8      11780.0   1.00      0.0         RUN68
-05                  0.014     299.8      11780.0   1.0       0.0         RUN68
```

```
069005                                                                        RUN69
311.0       300.66       152.0        300.66      0.7113       0.2887        RUN69
 961.1      972.2          89.72
001 117.0   192.84     16.0       299.8      23.79     0.5081    0.4919         RUN69
-02                    11.119     300.9      11780.0   0.6802    0.3198         RUN69
-03                    1.992      302.0      11780.0   0.7500    0.2500         RUN69
-04                    0.213      302.0      11780.0   1.0       0.0            RUN69
-05                    0.014      302.0      11780.0   1.0       0.0            RUN69

070004                                                                        RUN70
145.6       300.91       26.5         300.91      0.7115       0.2885        RUN70
 961.1      972.2          89.72
001 14.0    194.66     8.84       299.3      23.79     0.5415    0.4585         RUN70
-02                    8.856      302.0      11780.0   0.6977    0.3023         RUN70
-03                    1.006      301.5      11780.0   0.7500    0.2500         RUN70
-04                    0.014      301.5      11780.0   1.0       0.0            RUN70

071004                                                                        RUN71
762.5       297.9        543.0        297.9       0.0            1.0          RUN71
 961.1      972.2          89.72
001 492.0   192.16     56.0       297.6      23.79     0.0       1.0            RUN71
-02                    16.243     298.7      11780.0   0.0       1.0            RUN71
-03                    1.102      299.8      11780.0   0.0       1.0            RUN71
-04                    0.021      299.8      11780.0   0.0       1.0            RUN71

072004                                                                        RUN72
520.4       300.28       339.3        300.28      0.0            1.0          RUN72
 961.1      972.2          89.72
001 258.0   192.84     30.0       298.2      23.79     0.0       1.0            RUN72
-02                    12.878     300.4      11780.0   0.0       1.0            RUN72
-03                    1.568      302.0      11780.0   0.0       1.0            RUN72
-04                    0.073      302.0      11780.0   0.0       1.0            RUN72

073004                                                                        RUN73
323.2       300.0        175.2        300.0       0.0            1.0          RUN73
 961.1      972.2          89.72
001 113.5   192.84     30.0       297.6      23.79     0.0       1.0            RUN73
-02                    10.771     300.9      11780.0   0.0       1.0            RUN73
-03                    1.431      302.0      11780.0   0.0       1.0            RUN73
-04                    0.039      302.0      11780.0   0.0       1.0            RUN73

074004                                                                        RUN74
168.7       298.75        45.0         298.75        0.0          1.0         RUN 74
 961.1      972.2          89.72
001 42.0    192.84     25.0       298.7      23.79     0.0       1.0            RUN74
-02                    9.444      302.0      11780.0   0.0       1.0            RUN74
-03                    0.870      302.0      11780.0   0.0       1.0            RUN74
-04                    0.019      302.0      11780.0   0.0       1.0            RUN74

075005                                                                        RUN 75
742.3       300.4        498.6        300.4       0.7260       0.2740        RUN 75
 961.1      972.2          89.72
001 449.0   175.7      57.0       297.0      23.75     0.5791    0.4209         RUN 75
-02                    12.105     298.7      11780.0   0.6278    0.3723         RUN 75
-03                    6.226      298.7      11780.0   0.8760    0.1240         RUN 75
-04                    1.044      298.7      11780.0   1.0       0.0            RUN 75
-05                    0.07       298.7      11780.0   1.0       0.0            RUN 75

076004                                                                        RUN 76
328.2       300.4        155.7        300.4       0.7257       0.2743        RUN 76
 961.1      972.2          89.72
001 111.7   174.87     15.7       297.6      23.79     0.4908    0.5092         RUN 76
-02                    12.447     301.5      11780.0   0.6949    0.3051         RUN 76
-03                    1.799      302.1      11780.0   1.0       0.0            RUN 76
-04                    0.126      302.1      11780.0   1.0       0.0            RUN 76

077005                                                                        RUN 77
749.4       301.2        458.1        301.2       0.9990       0.0010        RUN 77
 961.1      972.2          89.72
001 420.0   173.2      60.0       297.6      23.79     0.9986    0.0014         RUN 77
-02                    13.652     299.8      11780.0   0.9984    0.0016         RUN 77
-03                    10.925     299.8      11780.0   1.0       0.0            RUN 77
-04                    1.856      300.4      11780.0   1.0       0.0            RUN 77
-05                    0.102      300.9      11780.0   1.0       0.0            RUN 77

078004                                                                        RUN 78
584.2       301.2        366.5        301.2       0.9995       0.0005        RUN 78
 961.1      972.2          89.72
001 331.0   175.2      48.0       299.8      23.79     0.9978    0.0022         RUN 78
-02                    14.232     302.1      11780.0   0.9931    0.0069         RUN 78
-03                    3.887      303.2      11780.0   1.0       0.0            RUN 78
-04                    0.435      303.2      11780.0   1.0       0.0            RUN 78

079004                                                                        RUN 79
348.4       299.2        172.8        299.2       0.9931       0.0069        RUN 79
 961.1      972.2          89.72
001 132.0   174.2      17.7       298.7      23.79     0.9883    0.0117       RUN 79
-02                    12.337     302.1      11780.0   0.9928    0.0072       RUN 79
-03                    2.398      302.1      11780.0   1.0       0.0          RUN 79
-04                    0.261      302.1      11780.0   1.0       0.0          RUN 79

080004                                                                        RUN80
165.8       300.4        24.4         300.4       0.9924       0.0076        RUN80
  961.1      986.9         89.72
001 7.4     173.2      7.37       298.7      23.79     0.9862    0.0138         RUN80
-02                    10.345     302.6      11754.0   1.0       0.0            RUN80
-03                    1.276      300.9      11754.0   1.0       0.0            RUN80
-04                    0.048      300.9      11754.0   1.0       0.0            RUN80

081006                                                                        RUN81
421.0       301.0        206.1        301.0       0.1779       0.8221        RUN81
 961.1      972.2          89.72
-01                    27.0       299.8      23.79     0.1766    0.8234         RUN81
002 173.4   123.2      24.0       300.9      23.79     0.0495    0.9505         RUN81
-03                    24.0       300.9      2.3       0.0500    0.9500         RUN81
-04                    13.748     302.6      11780.0   0.1348    0.8652         RUN81
-05                    3.539      300.9      11780.0   0.0       1.0            RUN81
-06                    0.261      298.7      11780.0   0.0       1.0            RUN81
```

```
082005                                                                    RUN 82
197.06        302.2        24.48        302.2        0.1805       0.8195  RUN 82
  961.2       984.9        89.72
001 18.7      122.0      18.38      299.8      23.79      0.0498   0.9502   RUN 82
-02                      12.240     303.2      11780.0    0.1694   0.8306   RUN 82
-03                      1.315      303.2      11780.0    0.0      1.0      RUN 82
-04                      0.097      303.2      11780.0    0.0      1.0      RUN 82
-05                      0.010      303.2      11780.0    0.0      1.0      RUN 82

084007                                                                    RUN 84
724.2         296.7        419.96       296.7        0.0          1.0     RUN 84
 961.1        972.2        89.72
001 364.7     123.0      100.0      298.0      0.0        0.0      1.0      RUN 84
002 374.8     123.0      100.0      298.0      0.0        0.0      1.0      RUN 84
003 369.8     122.0      41.0       296.5      23.79      0.0      1.0      RUN 84
-04                      18.525     299.8      11780.0    0.0      1.0      RUN 84
-05                      5.434      298.7      11780.0    0.0      1.0      RUN 84
-06                      1.740      298.7      11780.0    0.0      1.0      RUN 84
-07                      0.386      298.7      11780.0    0.0      1.0      RUN 84

085004                                                                    RUN 65
515.71        298.2        263.65       298.2        0.0          1.0     RUN 85
 961.1        972.2        89.72
001 258.7     123.0      36.56      297.6      23.79      0.0      1.0      RUN 85
-02                      17.694     300.9      11780.0    0.0      1.0      RUN 85
-03                      1.798      300.9      11780.0    0.0      1.0      RUN 85
-04                      0.126      300.9      11780.0    0.0      1.0      RUN 85

086005                                                                    RUN 86
404.84        299.7        185.96       299.7        0.0          1.0     RUN 86
 961.1        972.2        89.72
001 171.0     123.0      100.0      298.0      0.0        0.0      1.0      RUN 86
002 173.0     123.0      101.0      298.7      23.79      0.0      1.0      RUN 86
-03                      16.301     300.9      11780.0    0.0      1.0      RUN 86
-04                      1.160      300.9      11780.0    0.0      1.0      RUN 86
-05                      0.019      300.9      11780.0    0.0      1.0      RUN 86

087006                                                                    RUN 87
262.5         299.4        37.3         299.4        0.0          1.0     RUN 87
961.2         984.9        89.72                                          RUN 87
001 196.0     125.5      100.0      298.0      0.0        0.0      1.0      RUN 87
002 176.0     123.0      100.0      298.0      0.0        0.0      1.0      RUN 87
003 196.0     123.0      30.0       304.1      23.79      0.0      1.0      RUN 87
-04                      16.378     301.5      11780.0    0.0      1.0      RUN 87
-05                      1.470      301.5      11780.0    0.0      1.0      RUN 87
-06                      0.048      301.5      11780.0    0.0      1.0      RUN 87

088005                                                                    RUN 88
350.4         303.0        155.7        303.0        0.0          1.0     RUN 88
961.2         972.2        89.72                                          RUN 88
001 87.0      125.5      100.0      298.0      0.0        0.0      1.0      RUN 88
002 85.0      123.0      49.0       296.5      23.79      0.0      1.0      RUN 88
-03                      14.483     298.7      11780.0    0.0      1.0      RUN 88
-04                      1.102      299.8      11780.0    0.0      1.0      RUN 88
-05                      0.029      299.8      11780.0    0.0      1.0      RUN 88

089005                                                                    RUN 89
257.6         298.0        89.1         298.0        0.0          1.0     RUN 89
961.2         972.2        89.72                                          RUN 89
001 23.3      123.0      100.0      298.0      0.0        0.0      1.0      RUN 89
002 23.3      122.0      21.0       296.5      23.79      0.0      1.0      RUN 89
-03                      12.047     300.4      11780.0    0.0      1.0      RUN 89
-04                      1.682      298.7      11780.0    0.0      1.0      RUN 89
-05                      0.087      298.7      11780.0    0.0      1.0      RUN 89

090006                                                                    RUN 90
574.15        298.7        319.13       298.7        0.1818       0.8182  RUN 90
961.2         972.2        89.72                                          RUN 90
001 279.0     123.2      20.0       298.0      0.0        0.0511   0.9488   RUN 90
002 269.0     122.7      20.0       298.0      0.0        0.0511   0.9488   RUN 90
003 274.0     123.2      36.0       294.3      23.79      0.0511   0.9488   RUN 90
-04                      19.279     299.3      11780.0    0.1643   0.8357   RUN 90
-05                      0.889      299.3      11780.0    0.0      1.0      RUN 90
-06                      0.042      299.3      11780.0    0.0      1.0      RUN 90

091007                                                                    RUN 91
297.6         299.0        110.0        299.0        0.1855       0.8145  RUN 91
961.2         972.2        89.72                                          RUN 91
001 84.0      124.2      20.0       298.0      0.0        0.0466   0.9534   RUN 91
002 88.0      124.2      20.0       298.0      0.0        0.0466   0.9534   RUN 91
003 88.0      124.0      80.0       297.0      23.79      0.0466   0.9534   RUN 91
-04                      13.804     298.7      11780.0    0.1607   0.8393   RUN 91
-05                      1.624      298.7      11780.0    0.0      1.0      RUN 91
-06                      0.077      298.7      11780.0    0.0      1.0      RUN 91
-07                      0.004      298.7      11780.0    0.0      1.0      RUN 91

092007                                                                    RUN 92
411.0         298.2        255.0        298.2        0.9904       0.0096  RUN 92
961.2         972.2        89.72                                          RUN 92
001 166.0     200.2      20.0       298.0      0.0        0.9860   0.0140   RUN 92
002 136.0     192.2      20.0       298.0      0.0        0.9860   0.0140   RUN 92
003 161.0     200.2      115.0      297.0      23.79      0.9860   0.0140   RUN 92
-04                      11.879     299.3      11780.0    0.9917   0.0083   RON 92
-05                      1.760      299.3      11780.0    1.0      0.0      RUN 92
-06                      0.155      299.3      11780.0    1.0      0.0      RUN 92
-07                      0.014      299.3      11780.0    1.0      0.0      RUN 92
```

```
093005                                                                                  RUN 93
233.0           299.7         92.6          299.7           0.9895         0.0105       RUN 93
961.2           972.2          89.72                                                    RUN 93
001 43.0        192.9      20.0       298.0      0.0        0.9855     0.0145           RUN 93
002 37.0        191.5      33.0       298.2      23.79      0.9855     0.0145           RUN 93
-03                        10.887     300.4      11780.0    0.9910     0.0090           RUN 93
-04                        0.967      300.9      11780.0    1.0        0.0              RUN 93
-05                        0.039      300.9      11780.0    1.0        0.0              RUN 93

094004                                                                                  RUN 94
751.4           302.2         529.8         302.2           0.3528         0.6472       RUN 94
961.2           972.2          89.72                                                    RUN 94
001 490.0       196.9      52.0       300.9      23.79      0.2010     0.7990           RUN 94
-02                        16.746     303.2      11780.0    0.3528     0.6472           RUN 94
-03                        0.677      302.6      11780.0    0.0        1.0              RUN 94
-04                        0.029      302.6      11780.0    0.0        1.0              RUN 94

095004                                                                                  RUN 95
413.0           302.2         244.5         302.2           0.3448         0.6552       RUN 95
 961.1          972.2          89.72
001 195.0       195.9      43.0       298.7      23.79      0.1762     0.8238           RUN 95
-02                        12.898     300.9      11780.0    0.3310     0.6690           RUN 95
-03                        0.657      300.9      11780.0    1.0        0.0              RUN 95
-04                        0.029      300.9      11780.0    1.0        0.0              RUN 95

096004                                                                                  RUN 96
232.4           300.7         92.1          300.7           0.3457         0.6543       RUN 96
 961.1          972.2          89.72
001 70.0        194.2      69.0       296.5      23.79      0.1876     0.8124           RUN 96
-02                        10.248     300.4      11780.0    0.3317     0.6683           RUN 96
-03                        0.851      300.4      11780.0    1.0        0.0              RUN 96
-04                        0.048      300.4      11780.0    1.0        0.0              RUN 96

097004                                                                                  RUN 97
744.3           300.7         529.8         300.7           0.5455         0.4545       RUN 97
 961.1          972.2          89.72
001 420.0       194.7      102.0      298.7      23.79      0.3566     0.6434           RUN 97
-02                        15.585     299.8      11780.0    0.5250     0.4750           RUN 97
-03                        1.276      300.4      11780.0    1.0        0.0              RUN 97
-04                        0.058      300.4      11780.0    1.0        0.0              RUN 97

098005                                                                                  RUN 98
505.6           302.2         317.1         302.2           0.5405         0.4595       RUN 98
 961.1          972.2          89.72
001 287.0       195.2      66.0       298.2      23.79      0.3335     0.6665           RUN 98
-02                        13.768     299.8      11780.0    0.5202     0.4798           RUN 98
-03                        1.257      299.8      11780.0    1.0        0.0              RUN 98
-04                        0.081      299.8      11780.0    1.0        0.0              RUN 98
-05                        0.0097     299.8      11780.0    1.0        0.0              RUN 98

099004                                                                                  RUN 99
277.5           301.0         126.6         301.0           0.5340         0.4660       RUN 99
 961.1          972.2          89.72
001 102.6       195.2      94.0       297.6      23.79      0.3257     0.6743           RUN 99
-02                        11.428     299.3      11780.0    0.5289     0.4711           RUN 99
-03                        0.851      299.3      11780.0    1.0        0.0              RUN 99
-04                        0.035      299.8      11780.0    1.0        0.0              RUN 99

100005                                                                                  RUN100
660.0           299.2         463.0         299.2           0.8123         0.1877       RUN100
 961.1          972.2          89.72
001 358.0       195.2      81.0       297.0      23.79      0.6873     0.3127           RUN100
-02                        15.276     299.8      11780.0    0.8062     0.1938           RUN100
-03                        1.102      299.8      11780.0    1.0        0.0              RUN100
-04                        0.058      299.8      11780.0    1.0        0.0              RUN100
-05                        0.0039     299.8      11780.0    1.0        0.0              RUN100

101005                                                                                  RUN101
432.0           299.0         257.6         299.0           0.8156         0.1844       RUN101
 961.1          972.2          89.72
001 205.5       194.7      67.0       298.7      23.79      0.6582     0.3418           RUN101
-02                        12.956     300.4      11780.0    0.7842     0.2158           RUN101
-03                        1.392      300.4      11780.0    1.0        0.0              RUN101
-04                        0.073      300.4      11780.0    1.0        0.0              RUN101
-05                        0.015      300.4      11780.0    1.0        0.0              RUN101

102005                                                                                  RUN102
245.5           299.7         99.2          299.7           0.8138         0.1862       RUN102
 961.1          972.2          89.72
001 66.0        196.2      51.7       298.7      23.79      0.7003     0.2997           RUN102
-02                        10.829     301.5      11780.0    0.8058     0.1942           RUN102
-03                        1.044      301.5      11780.0    1.0        0.0              RUN102
-04                        0.056      301.5      11780.0    1.0        0.0              RUN102
-05                        0.0097     301.5      11780.0    1.0        0.0              RUN102

103004                                                                                  RUN103
235.4           301.2         160.7         301.2           0.0349         0.9651       RUN103
 961.1          972.2          89.72
001 155.0       295.9      132.5      297.6      23.79      0.0007     0.9993           RUN103
-02                        5.356      300.9      11780.0    0.0        1.0              RUN103
-03                        0.213      300.9      11780.0    0.0        1.0              RUN103
-04                        0.014      300.9      11780.0    0.0        1.0              RUN103

104005                                                                                  RUN104
643.6           301.2         502.6         301.2           0.3900         0.6100       RUN104
 961.1          972.2          89.72
001 488.0       300.9      50.7       299.8      23.79      0.2801     0.7199           RUN104
002 450.0       295.7      82.0       302.1      23.79      0.2712     0.7288           RUN104
-03                        10.016     305.2      11780.0    0.3828     0.6172           RUN104
-04                        0.348      305.2      11780.0    1.0        0.0              RUN104
-05                        0.019      305.2      11780.0    1.0        0.0              RUN104
```

```
105004                                                                   RUN105
476.4        304.0        358.5         304.0        0.3887       0.6113      RUN105
 961.1       972.2          89.72
001 319.0    296.7     134.5    302.1     61.94      0.2738    0.7262         RUN105
-02                    8.044    302.6     11780.0    0.3845    0.6155         RUN105
-03                    0.348    302.6     11780.0    1.0       0.0            RUN105
-04                    0.014    302.6     11780.0    1.0       0.0            RUN105

106004                                                                   RUN106
226.3        302.9        149.6         302.9        0.3881       0.6119      RUN106
 961.1       972.2          89.72
001 134.0    296.4     81.8     302.1     23.79      0.2698    0.7302         RUN106
-02                    5.588    302.1     11780.0    0.3776    0.6224         RUN106
-03                    0.251    302.1     11780.0    1.0       0.0            RUN106
-04                    0.0097   302.1     11780.0    1.0       0.0            RUN106

107004                                                                   RUN 107
448.2        303.2        335.3         303.2        0.2226       0.7774      RUN 107
 961.1       972.2          89.72
001 309.7    296.7     63.0     304.1     23.79      0.1495    0.8505         RUN 107
-02                    8.121    303.2     11780.0    0.2121    0.7879         RUN 107
-03                    0.329    303.2     11780.0    0.0       1.0            RUN 107
-04                    0.014    303.2     11780.0    0.0       1.0            RUN 107

108004                                                                   RUN 108
210.2        298.9        139.5         298.9        0.2122       0.7878      RUN 108
 961.1       972.2          89.72
001 123.3    296.4     40.0     302.6     23.79      0.1489    0.8511         RUN 108
-02                    5.337    303.2     11780.0    0.2165    0.7835         RUN 108
-03                    0.193    303.2     11780.0    0.0       1.0            RUN 108
-04                    0.0096   303.2     11780.0    0.0       1.0            RUN 108

109004                                                                   RUN 109
682.9        302.9        532.8         302.9        0.2533       0.7467      RUN 109
 961.1       972.2          89.72
001 520.2    296.2     45.0     300.4     23.79      0.1714    0.8286         RUN 109
-02                    10.132   302.1     11780.0    0.2496    0.7504         RUN 109
-03                    0.483    302.1     11780.0    0.0       1.0            RUN 109
-04                    0.021    302.1     11780.0    0.0       1.0            RUN 109

110004                                                                   RUN 110
415.9        300.4        310.0         300.4        0.2583       0.7417      RUN 110
 961.1       972.2          89.72
001 288.7    296.2     52.0     302.6     23.79      0.1731    0.8269         RUN 110
-02                    7.870    303.2     11780.0    0.2405    0.7595         RUN 110
-03                    0.348    303.2     11780.0    0.0       1.0            RUN 110
-04                    0.015    303.2     11780.0    0.0       1.0            RUN 110
 111004                                                                  RUN 111
 296.9        303.0        206.1         303.0        0.2589       0.7411     RUN 111
  961.1       972.2          89.72
 001 188.5    296.2     50.8     301.5     23.79      0.1741    0.8259        RUN 111
 -02                    6.613    303.2     11780.0    0.2474    0.7526        RUN 111
 -03                    0.309    303.2     11780.0    0.0       1.0           RUN 111
 -04                    0.012    303.2     11780.0    0.0       1.0           RUN 111

 112005                                                                  RUN112
 1365.0       302.2        1055.0        302.2        0.0          1.0        RUN112
 961.7        972.7        89.72                                              RUN112
 001 850.0    197.5     95.0     303.2     23.79      0.0011    0.9989        RUN112
 -02                    20.304   303.2     11780.0    0.0009    0.9991        RUN112
 -03                    3.616    303.2     11780.0    0.0       1.0           RUN112
 -04                    0.348    303.2     11780.0    0.0       1.0           RUN112
 -05                    0.004    303.2     11780.0    0.0       1.0           RUN112

 113004                                                                  RUN113
 1005.0       304.4        742.0         304.4        0.0012       0.9988     RUN113
 961.7        972.7        89.72                                              RUN113
 001 660.0    197.5     80.0     305.2     23.79      0.0016    0.9984        RUN113
 -02                    18.000   305.8     11780.0    0.0012    0.9988        RUN113
 -03                    0.948    305.8     11780.0    0.0       1.0           RUN113
 -04                    0.019    305.8     11780.0    0.0       1.0           RUN113

 114005                                                                  RUN114
 755.0        298.2        539.5         298.2        0.9915       0.0085     RUN114
 961.7        972.7        89.72                                              RUN114
 001 460.0    195.0     55.0     297.6     23.79      0.9873    0.0127        RUN114
 -02                    16.417   298.2     11780.0    0.9874    0.0126        RUN114
 -03                    3.461    298.2     11780.0    1.0       0.0           RUN114
 -04                    0.252    298.2     11780.0    1.0       0.0           RUN114
 -05                    0.019    298.2     11780.0    1.0       0.0           RUN114

 115004                                                                  RUN115
 910.0        296.2        755.0         296.2        0.9913       0.0087     RUN115
 961.7        972.7        89.72                                              RUN115
 001 750.0    297.9     80.0     297.6     23.79      0.9877    0.0123        RUN115
 -02                    12.762   298.2     11780.0    0.9884    0.0116        RUN115
 -03                    0.793    298.2     11780.0    1.0       0.0           RUN115
 -04                    0.038    298.2     11780.0    1.0       0.0           RUN115
```

```
116004                                                                    RUN116
1585.0       295.4       1243.0       295.4        0.0          1.0       RUN116
961.7        972.7       123.6                                            RUN116
001 1290.0   191.2     15.0      297.6     0.0        0.0       1.0       RUN116
-02                    24.152    299.6     11780.0    0.0       1.0       RUN116
-03                    0.425     297.6     11780.0    0.0       1.0       RUN116
-04                    0.019     297.6     11780.0    0.0       1.0       RUN116

117004                                                                    RUN117
885.0        295.7       698.0        295.7        1.0          0.0       RUN117
961.7        972.7       123.6                                            RUN117
001 625.0      192.5     15.0      297.0     0.0        1.0       0.0     RUN1 7
-02                    17.171    297.0     11780.0    1.0       0.0       RUN117
-03                    0.309     297.0     11780.0    1.0       0.0       RUN117
-04                    0.019     297.0     11780.0    1.0       0.0       RUN117

118004                                                                    RUN118
525.0        300.0       328.0        300.0        0.7360       0.2640    RUN118
 961.2       972.2        89.7                                            RUN118
001 251.0    175.0     30.0      297.0     23.7       0.5489    0.4511    RUN118
-02                    12.5      298.0     11780.0    0.6298    0.3703    RUN118
-03                    3.5       298.0     11780.0    1.0       0.0       RUN118
-04                    1.5       298.0     11780.0    1.0       0.0       RUN118

120004                                                                    RUN 120
 469.0       298.2       370.0        298.2        0.0          1.0
 961.7       972.7       88.91                                            RUN 120
001 312.0    298.4     27.0      300.9     23.79      0.0         1.0     RUN 120
-02                    7.851     297.7     11780.0    0.0         1.0     RUN 120
-03                    0.715     297.7     11780.0    0.0         1.0     RUN 120
-04                    0.019     297.7     11780.0    0.0         1.0     RUN 120

121006                                                                    RUN121
 174.0        296.7      117.0        296.7         0.0         1.000     RUN121
 961.7       972.7        88.91                                           RUN121
001 99.6     297.9     10.0      302.6     0.0        0.0       1.000     RUN121
002  94.0    295.9     10.0      302.6     0.0        0.0       1.00      RUN121
003 99.6     297.2     90.0      302.6     26.0       0.0       1.0       RUN121
-04                    4.351     298.8     11780.0    0.0       1.0       RUN121
-05                    0.193     298.8     11780.0    0.0       1.0       RUN121
-06                    0.004     299.3     11780.0    0.0       1.0       RUN121

122005                                                                    RUN 122
553.0        298.2       429.0         298.2       1.0          0.0       RUN 122
 961.7       972.7        88.91                                           RUN 122
001 330.8    295.9     39.0      300.0     0.0        1.0       0.0       RUN 122
002 326.0    293.4     39.0      299.3     23.79      1.0       0.0       RUN 122
-03                    10.596    298.8     11780.0    1.0       0.0       RUN 122
-04                    0.406     298.8     11780.0    1.0       0.0       RUN 122
-05                    0.014     298.8     11780.0    1.0       0.0       RUN 122

123004                                                                    RUN 123
217.00       299.7       125.0        299.7          1.0        0.0       RUN 123
 961.7        972.7      88.91                                            RUN 123
001 94.0     295.7     85.0      298.7     23.79      1.0       0.0       RUN 123
-02                    6.052     297.6     11780.0    1.0       0.0       RUN 123
-03                    0.367     297.6     11780.0    1.0       0.0       RUN 123
-04                    0.014     297.6     11780.0    1.0       0.0       RUN 123

124005                                                                    RUN124
265.0        293.9       170.0        293.9        1.0          0.0       RUN124
961.2        972.7       88.91                                            RUN124
001 115.0    296.4     30.0      297.61    0.0        1.0       0.0       RUN124
002 145.0    296.4     30.0      297.61    23.79      1.0       0.0       RUN124
-03                    7.31      297.1     11780.0    1.0       0.0       RUN124
-04                    0.406     297.1     11780.0    1.0       0.0       RUN124
-05                    0.029     297.1     11780.0    1.0       0.0       RUN124
```

APPENDIX B

CALIBRATIONS

TABLE XX

THERMOCOUPLE CALIBRATION DATA

Reference Point	Reference Temperature °C	Thermocouple Reading Average* EMF. MV.	Average* Temp. °C (38 Calib)	Average Deviation
Boiling H_2O (739.5 mm Hg)	99.2	4.25	99.4	0.2
Ice Point	0	0.0	0	0.0
CO_2 Sublimation Point	-78.5	-2.71	-78.25	0.25
Boiling O_2	-182.96	-5.25	-182.5	0.46
Boiling N_2	-195.8	-5.47	-195.5	0.30

* 5 readings each at each point.

\- - - - - - - -

TABLE XXI

CALIBRATION DATA FOR PRESSURE GAUGES

Dead Weight Tester PSIG		Gauge Readings PSIG Up	Down
	Gauge C-2-522		
50			75
100		120	125
200		220	225
300		325	325
400		420	425
500		520	525
750		800	805
1000		1050	1055
1100		1160	1165
1250		1305	1305
1350		1410	1415
1500		1585	1585
1750		1820	
	Gauge C-2-464		
20		27	26
30		36	37
40		48	50
60		67	69
80		85	88
110		117	117
160		165	165
210		215	216
260		265	266
310		316	318
410		415	416
510		518	519
560		570	
	Gauge C-2-82		
20		26	26
40		48	47
80		86	85
110		116	117
210		215	

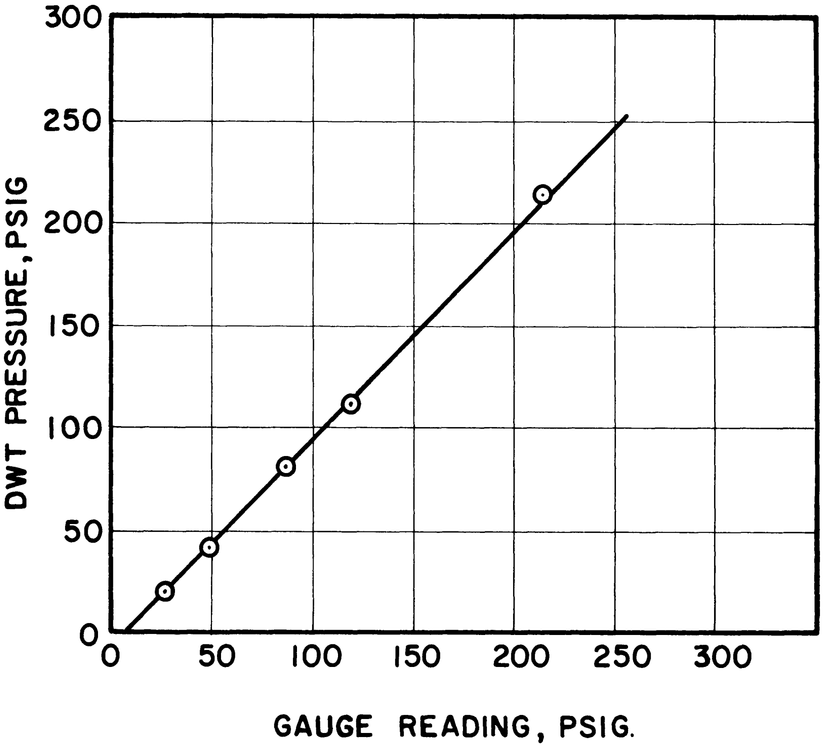


Figure 21. Calibration of 300 Psi Pressure Gauge (C-2-82).

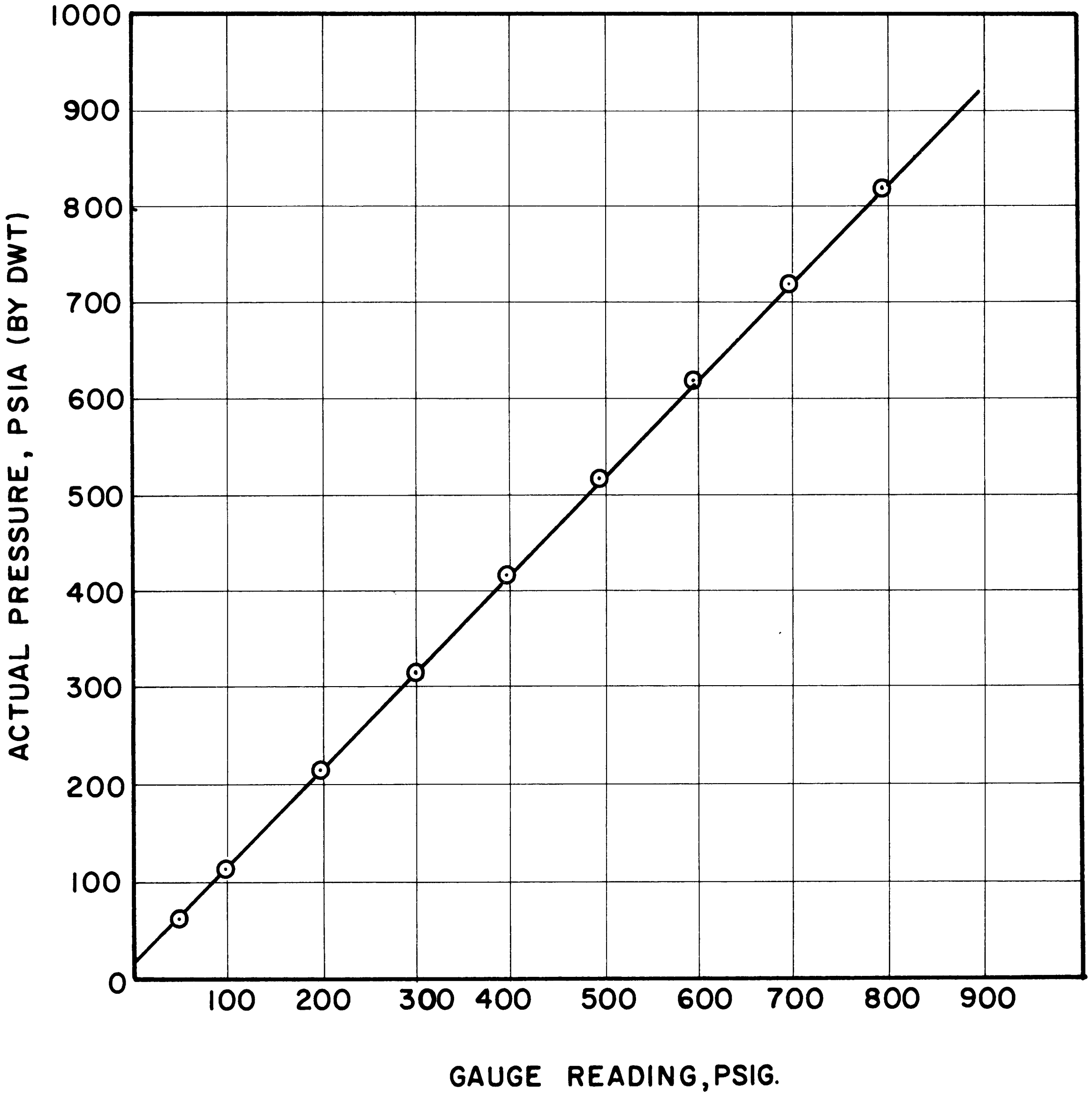


Figure 22. Calibration for 800 Psi Pressure Gauge (No. C-2-464).

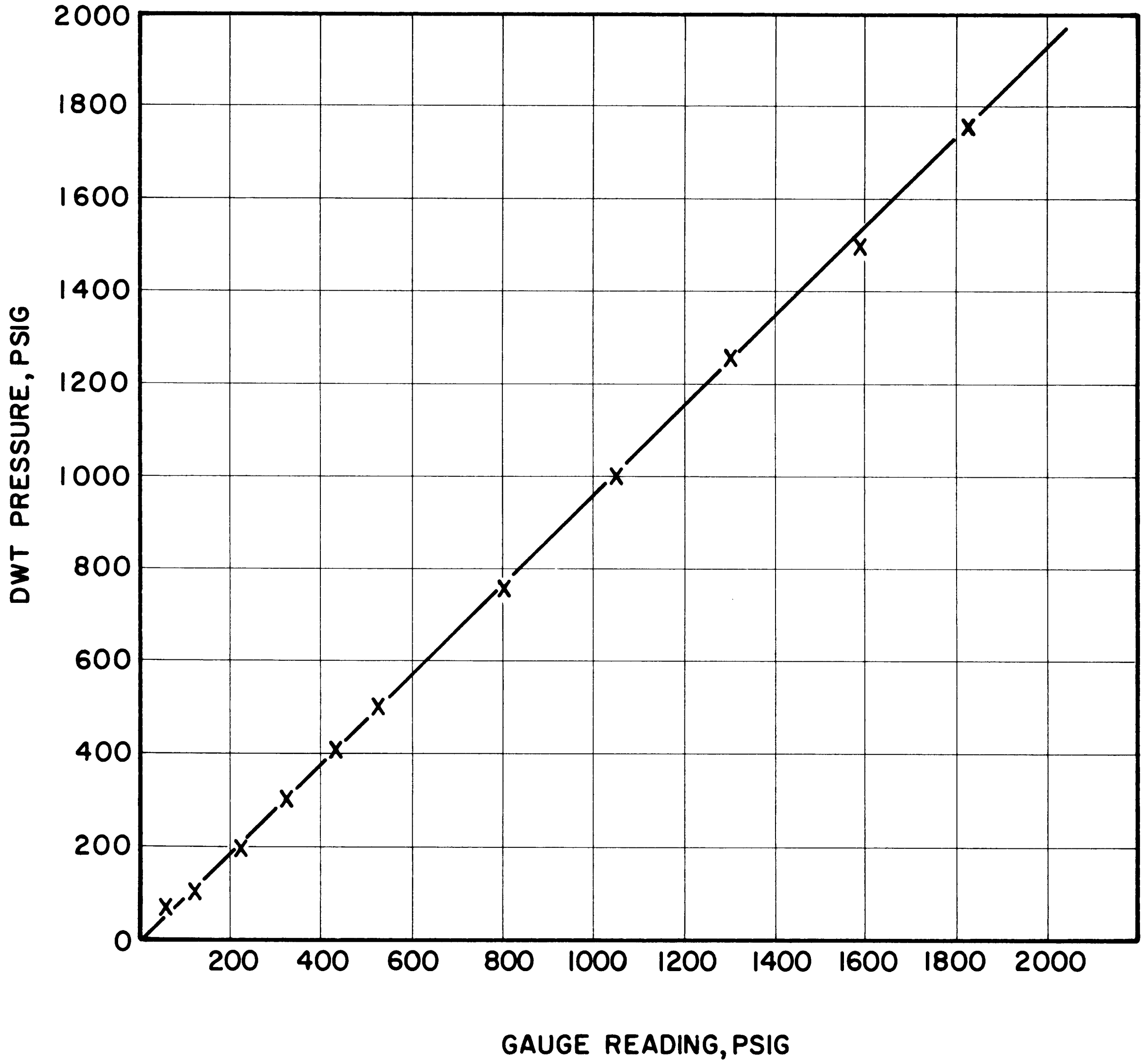


Figure 23. Calibration for 2000 Psi Pressure Gauge (No. C-2-522).

TABLE XXII

CALIBRATION DATA FOR 2000 PSI PRESSURE TRANSDUCER
(Serial No. 110)

Temperature: 26°C Reference Pressure: 0.01mm Hg.

GAUGE READING PSIA	TRANSDUCER READING MV
290	7.75
1215	36.5
1305	39.0
955	28.5
760	22.5
570	16.75
475	13.5
375	10.5
205	5.0
260	6.25
450	12.5
290	7.75

\- - - - - - - - - -

TABLE XXIII

CALIBRATION OF 2000 PSI PRESSURE TRANSDUCER
(Serial No. 110)

Temperature: 79.6°C   Reference Pressure: 0.01mm Hg

GAUGE READING PSIA	TRANSDUCER READING MV
1435	39.0
1140	30.8
1055	27.5
932	25.0
741	20.0
612	16.0
360	9.2
245	6.0
162	4.0
87	2.0
1100	29.5
913	24.8
815	22.0
665	18.0
550	14.4
430	11.2
330	8.4
220	5.4
180	4.5
325	8.4
450	11.8
573	15.0
680	18.0
645	17.0
965	27.0
1419	39.2
1320	36.5
1050	29.0
945	26.0
680	21.0
620	16.7
455	12.2
240	6.0
180	4.6

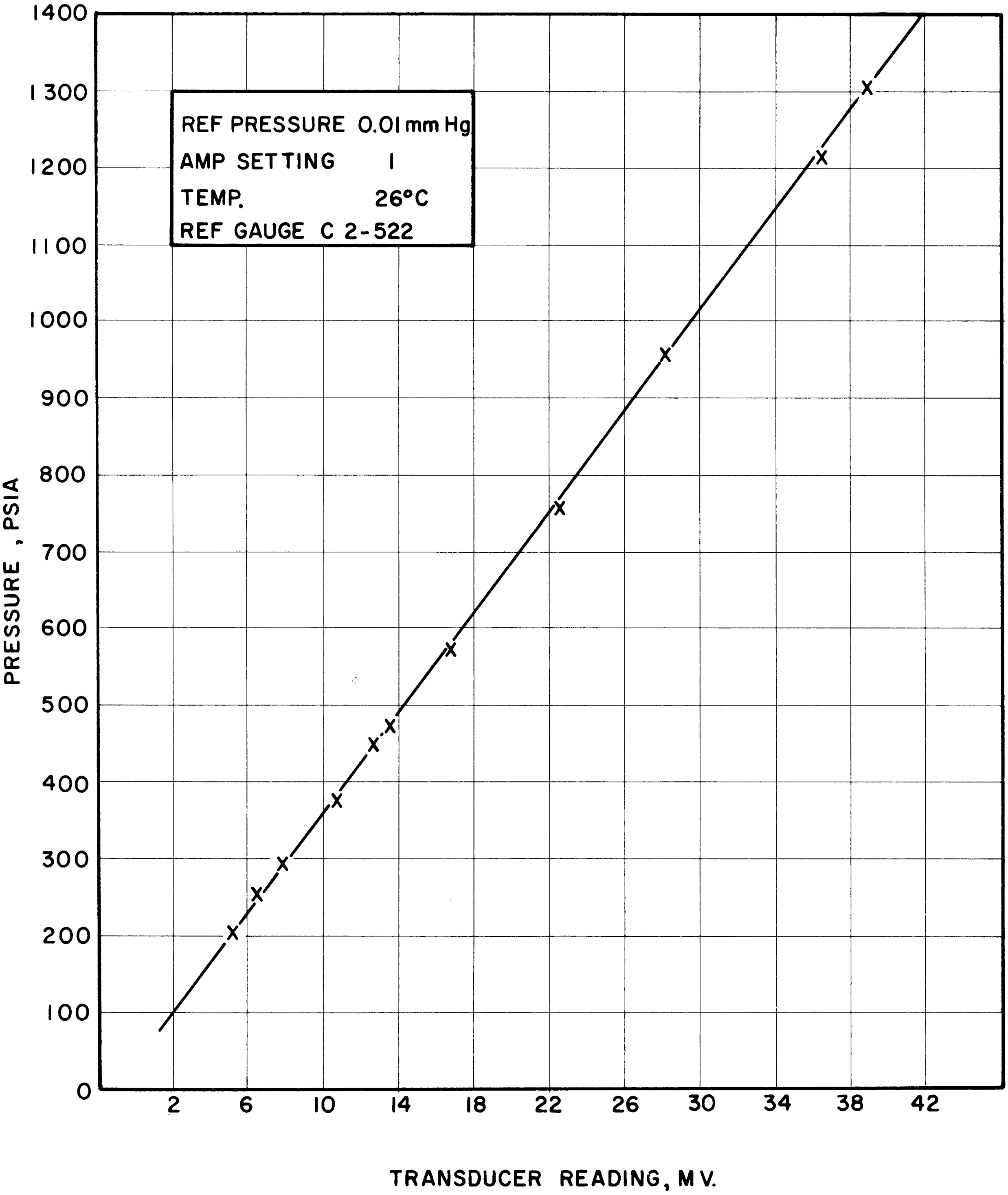


Figure 24. Calibration for 2000 Psi Pressure Transducer (Serial No. 110).

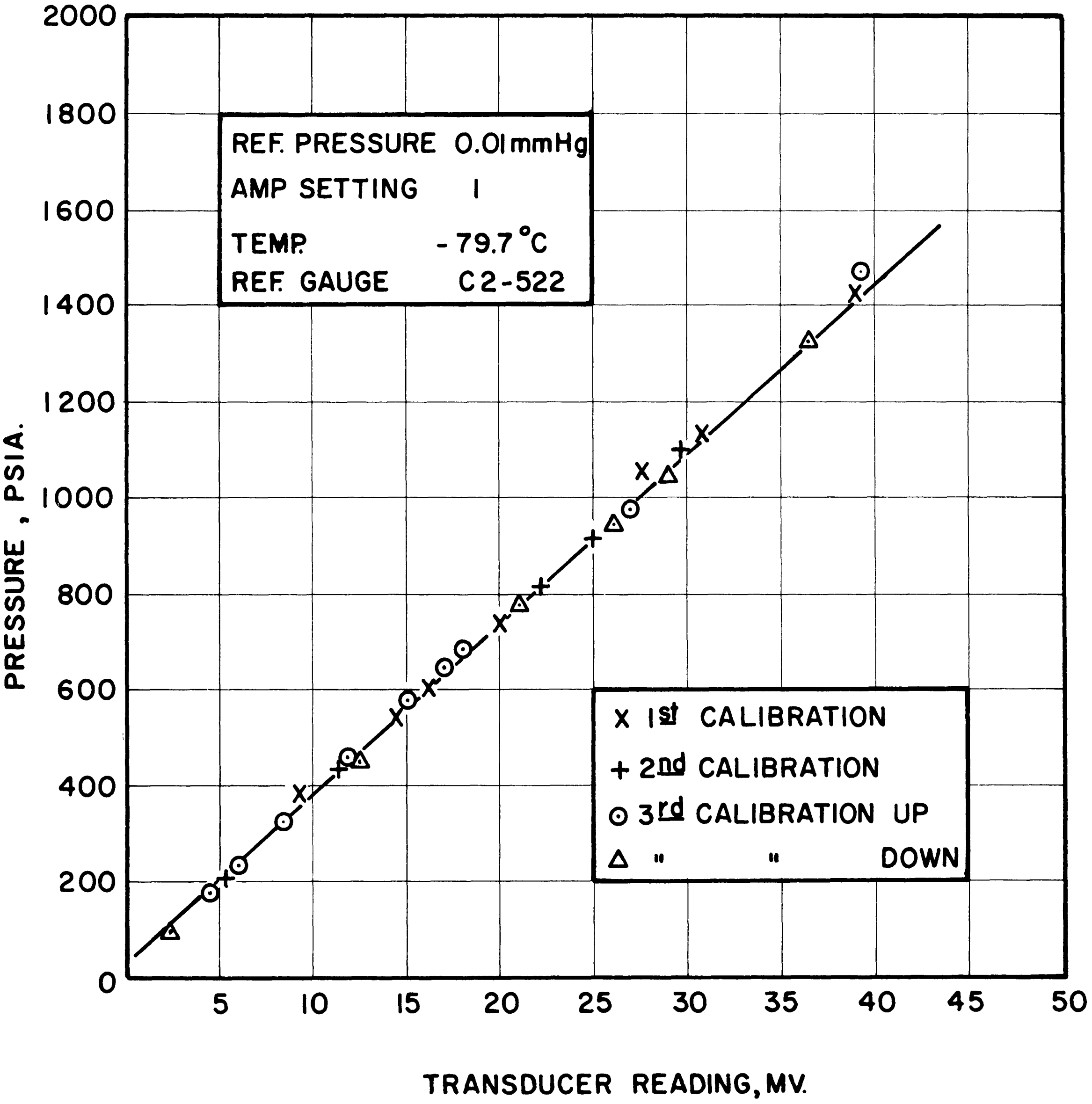


Figure 25. Calibration for 2000 Psi Pressure Transducer (Serial No. 110).

TABLE XXIV

CALIBRATION DATA FOR
500 PSI PRESSURE TRANSDUCER
(Serial No. 60)

Gauge Reading PSIA	Transducer Reading MV
Temperature: -79.7°C	Reference Pressure: 0.01mm Hg
115	13.5
218	24.0
321	33.5
423	43.5
523	53.0
621	63.0
656	67.0
566	57.0
519	52.5
420	44.0
368	39.0
320	33.5
216	23.9
150	17.7
119	14.0
67	8.4
421	44.0
115	13.2
Temperature: 20°C	Reference Pressure: 0.01mm Hg
138	16
256	25.5
254	25.0
419	45.0
455	49.0
322	35.0
218	24.0
138	15.6
67	8.0

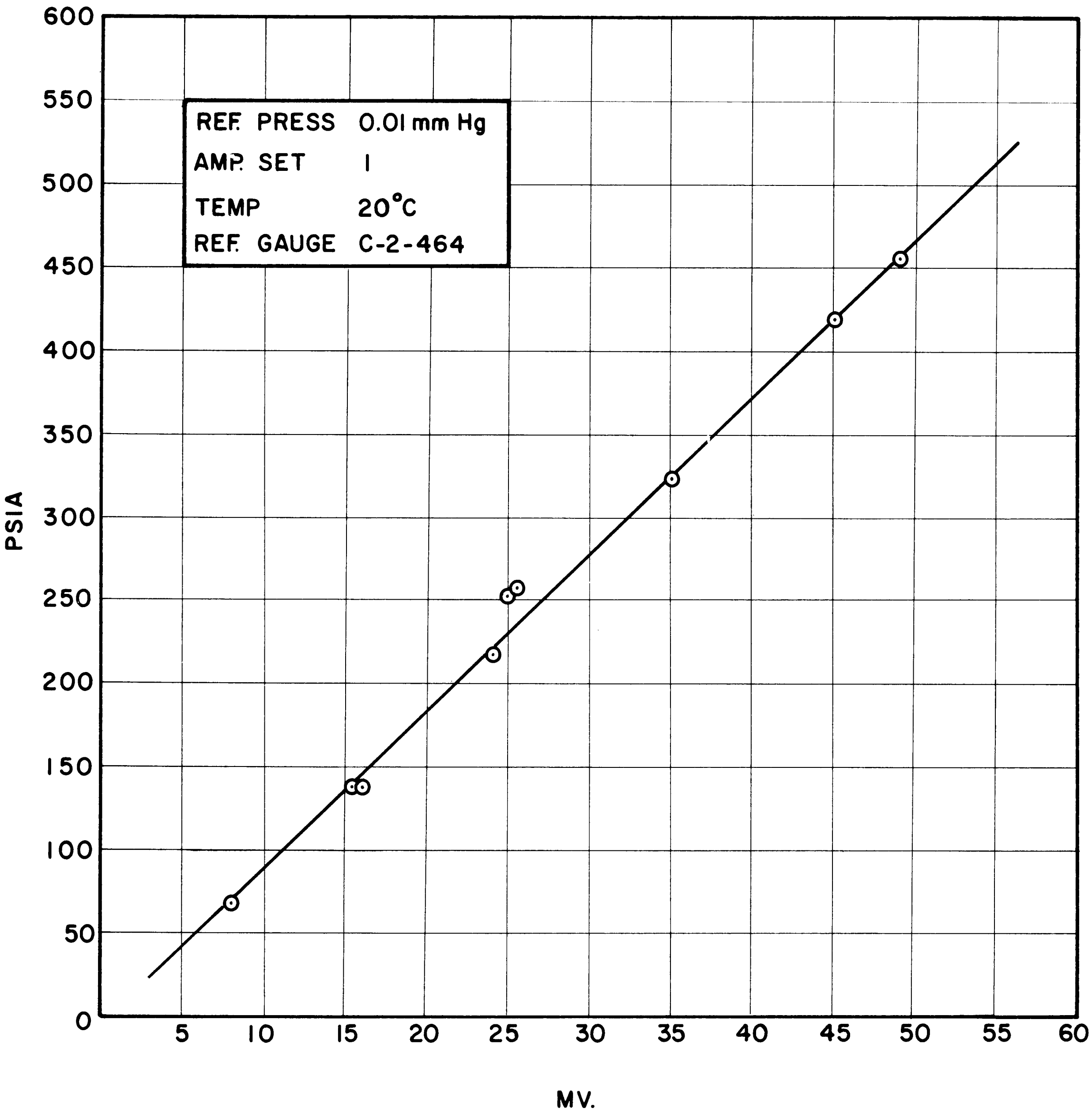


Figure 26. Calibration for 500 Psi Pressure Transducer. (Serial No. 60)

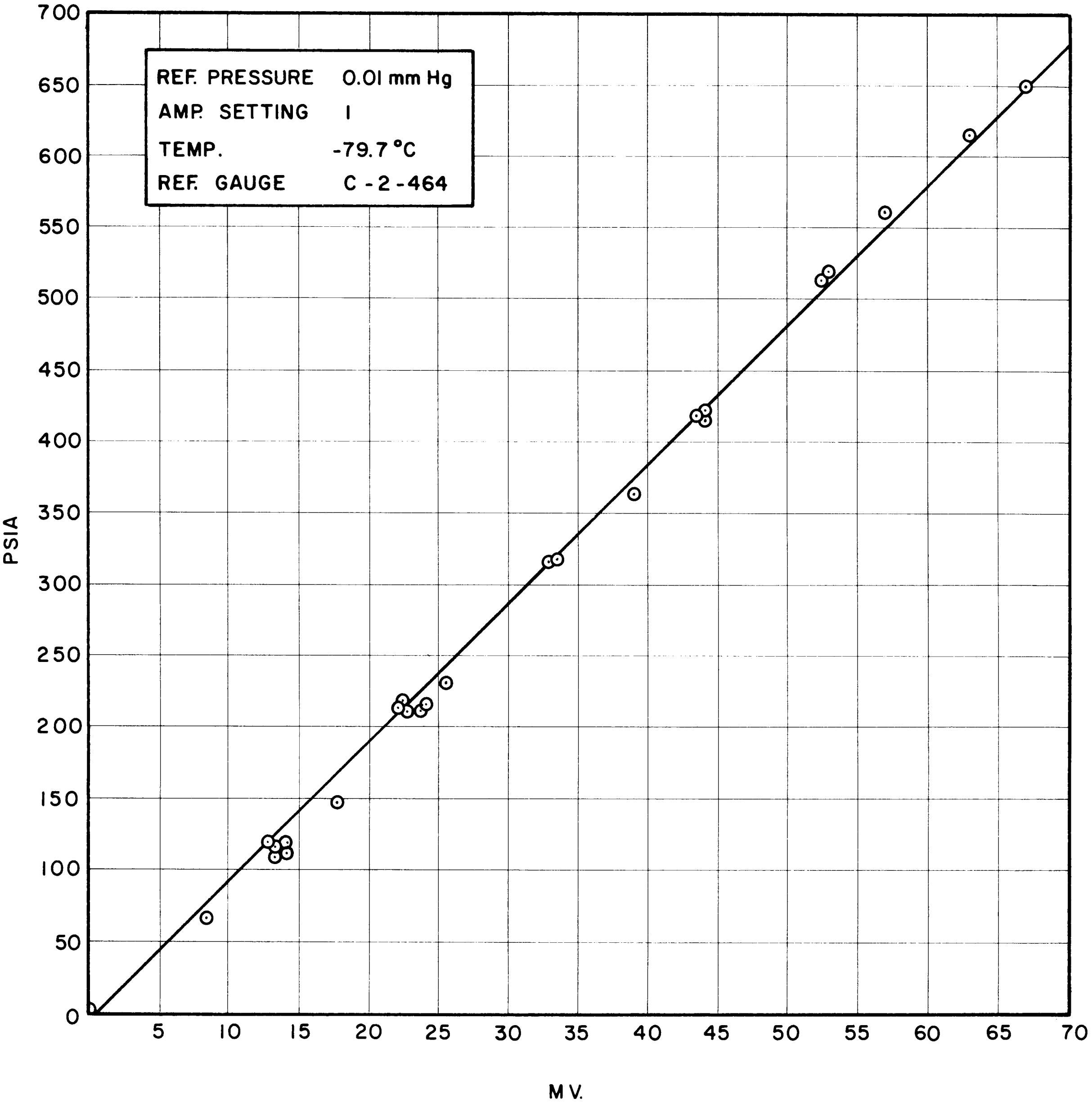


Figure 27. Calibration for 500 Psi Pressure Transducer.
(Serial No. 60)

APPENDIX C

CALCULATION OF SURFACE AREA

Two determinations of the surface area of the adsorbent were made using the standard "BET" method. The first was made after activating the adsorbent for 12 hours at 350°C under a vacuum of 10^{-6} mm. of Hg. For the second determination, the sample was activated at 125°C for 12 hours at 3×10^{-2} mm. Hg. pressure. The results were essentially identical being 494 and 512 square meters per gram for the respective "BET" determinations. The calculated data may be found in Tables XXV and XXVI and Figures 28 and 29.

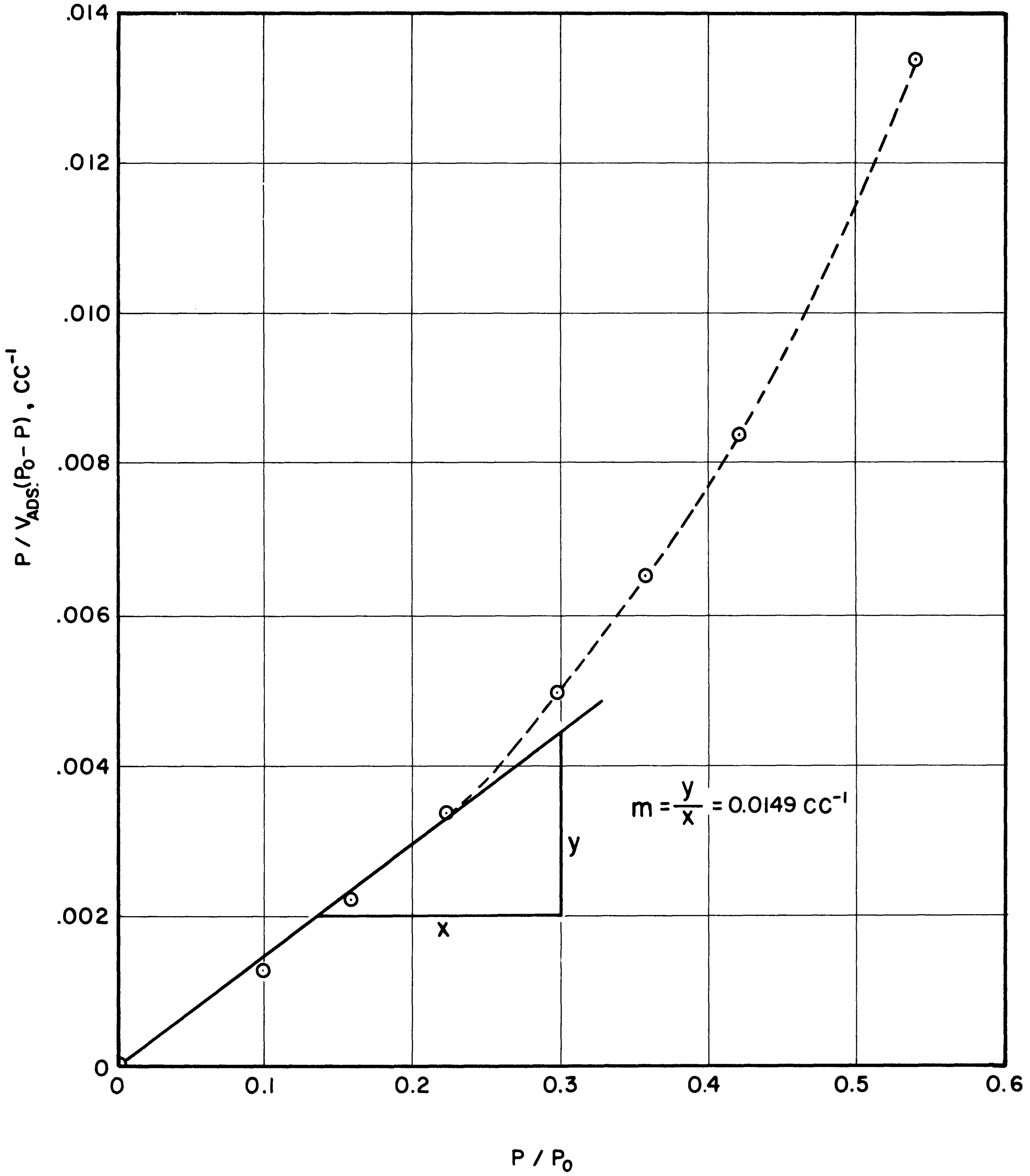


Figure 28. "B E T" Plot for Surface Area

Determination 1

Sample - 5A Molecular Sieve

TABLE XXVI

CALCULATION OF BET SURFACE AREA DETERMINATION
DETERMINATION 2

Activation Temperature = 125°C
Activation Pressure = 3×10^{-2} mm Hg
Weight of Sample = 0.3023 gms.
Average Adsorption Temperature = 193.5°C

DATA

Readings	Pressure mm Hg.	P-Po mm Hg	V Ads ccSTP	P/V Ads(P-Po)	P/Po
1	23.0	712.3	39.5	0.00083	0.031
2	32.0	703.3	39.54	0.00115	0.044
3	41.0	694.3	39.77	0.00148	0.056
4	50.0	685.3	40.02	0.00182	0.068
5	59.5	675.8	40.25	0.00219	0.081
6	78.5	656.8	40.53	0.00295	0.107
7	100.5	634.8	40.68	0.00389	0.137
8	147.5	587.8	41.20	0.00609	0.201
9	206.5	529.3	41.60	0.00936	0.280
10	255.0	480.3	41.83	0.01269	0.347
11	298.0	437.3	42.25	0.01617	0.405
12	398.0	337.3	43.03	0.02742	0.541

$m = 0.0282\,cc^{-1}$ (From Figure 29)

$I = 0.00\,cc^{-1}$

$$v_m = \frac{1}{I + m} = 34.46 \text{ cc}$$

$$\text{Total Surface Area} = \frac{(34.46\text{cc})(6.02\times10^{23})(16.2)}{(22{,}400)(10^{10})^2} = 154.4 \text{ sq. meters}$$

$$\text{Specific Surface} = \frac{154.4 \text{ sq. meters}}{0.3023 \text{ gms}} = 511 \text{ sq. meters/gm.}$$

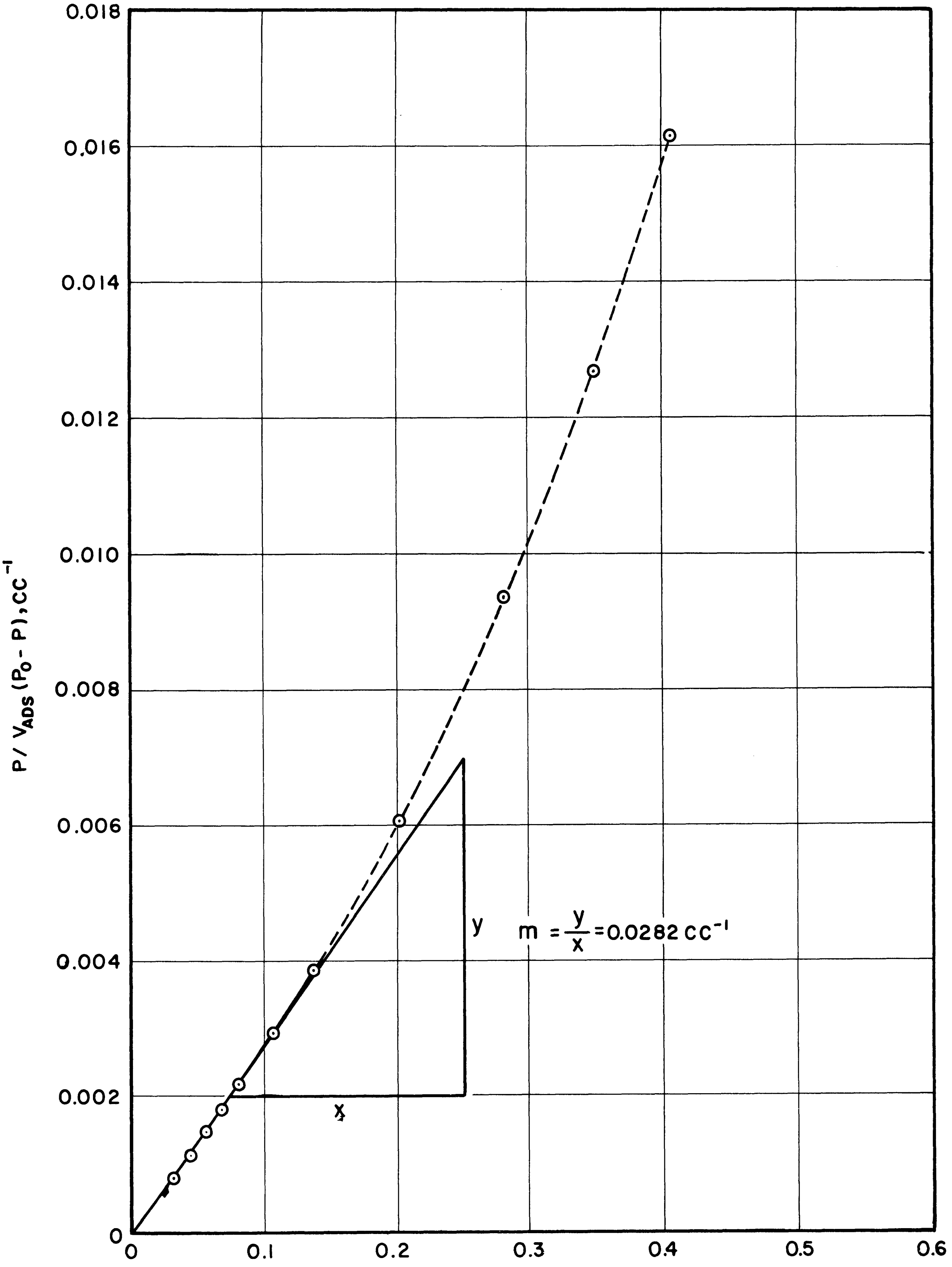


Figure 29. "B E T" Plot for Surface Area Determination 2

Sample - 5A Molecular Sieve

APPENDIX D

PRESSURE VESSEL DESIGN CALCULATIONS

A. Design Calculation

Using the thick-walled formula from the Unfired Pressure Vessel Code for computing the allowable working pressure (Para. VA-1)

$$P = SE(^{z-1}/z+1)$$

where

$Z = (R_o/R_o - t)^2$

E = Weld efficiency = 1.0 for seamless tube

P = allowable pressure

R_o = outside radius (in.) = 1.9 in

S = allowable stress (psi) = 18,750 psi

t = thickness (in.) = 0.4 in.

Then

$$Z = (0.95/0.95-0.4)^2 = 2.99$$

$$P = 18{,}750 \times 1.0(2.99 - 1/2.99 + 1)$$

$$P = 9{,}350 \text{ psi.}$$

For the end design the Code (Para. UG - 34) specifies that for flat heads the thickness shall be determined using:

$$t = d\sqrt{CP/S}$$

where

t = minimum thickness

d = the inside diameter

c = appropriate constant = 0.25

as the criteria.

Then $t = 1.1\sqrt{0.25 \times 9{,}350/18{,}750}$

$= 0.125$ inches minimum

B. Effect of Temperature and Pressure on Free Volume

The effect on the calibrated volume of the absorption cell by both high pressures and low temperatures may be considerable.

Bartlett(5) found that:

$$\Delta V = \frac{V_o}{E(r_2^2 - r_1^2)} [(1-2u)(P_2r_2^2 - P_1r_1^2) + 2(1+u)(P_2-P_1)r_2^2]$$

where

V_o = 124 cc. at 1 atm.

$E = 29.3 \times 10^6$ lbs./in.^{2}

$u = 0.28$

$r_1 = 1.1''$

$r_2 = 1.9''$

P_2 = operating pressure

P_1 = test pressure

represents the effect of pressure on the volume of a vessel at constant temperature. Calculations indicate that the change of volume resulting from a maximum operating pressure of 2000 psi, is 0.050 cc. or 0.04%.

The effect of a change of temperature on the volume of the adsorption cell was determined using the standard volumetric expansion equation:

$$V_{T_2} = V_{T_1}[1 + 3x\alpha(T_2 - T_1)]$$

where the linear coefficient of expansion

$\alpha = 16\text{x}10^{-6}\ {}^\circ C^{-1}$ for 316 stainless steel.

The minimum operating temperature of 123°K resulted in a change of 0.9 per cent in the volume.

As the total change resulting from the maximum change in the operating conditions is less than one per cent, the approximate error in the calibration, no correction was made for temperature and pressure.

APPENDIX E

SAMPLE CALCULATION OF ADSORPTION EQUILIBRIUM

Sample Calculation

Run No. 76

A. Calculation of Gas Density by B-W-R Equation at Initial Feed Conditions

Experimental Data

$$P = 328.2 \text{ psia}$$

$$T = 300.4°\text{K}$$

$$Y_{CH_4} = 0.7257$$

Calculation

$$P = \frac{328.2}{14.696} = 22.33 \text{ atm.}$$

Mixed Coefficients

$$B_{om}(\text{BM})^* = \sum_i B_{oi} y_i$$

$$= 0.0426000 \times 0.7257 + 0.0484824 \times 0.2743$$

$$= 0.0442135$$

$$A_{om}(\text{AM}) = (\sum_i A_{oi}^{\frac{1}{2}} y_i)^2 - 0.1000\ (y_{CH_4} \times y_{N_2})$$

$$= ((1.8550)^{\frac{1}{2}} \times 0.7257 + (1.27389)^{\frac{1}{2}} \times 0.2743)^2$$

$$- 0.1\ (0.7257 \times 0.2743)$$

$$= 1.6648$$

C_{om}(CM), D_{om}(DM) and γ_m(IM) follow squared combinatorial rule, without the added correction. Thus:

$$C_{om}(\text{CM}) = ((22570.0)^{\frac{1}{2}} \times 0.7257 + (4273.0)^{\frac{1}{2}} \times 0.2743)^2$$

$$= 16{,}648.6$$

---

* The letters in parentheses are used in the computer program.

$$D_{om}(DM) = (7.61781 \times 10^6) \times (0.2743)^2$$

$$= 5.73168 \times 10^5$$

$$\gamma_m(IM) = ((0.006000)^{\frac{1}{2}} \times 0.7257 + (0.006500)^{\frac{1}{2}} \times 0.2743)^2$$

$$= 0.006135$$

$$b_m(EM) = (\sum_i b_i^{1/3} y_i)^3$$

$$= ((0.00338004)^{1/3} \times 0.7257 + (0.00232373)^{1/3}$$

$$\times 0.2743)^3$$

$$= 0.00306385$$

$a_m(FM)$, $c_m(GM)$, $\delta_m(HM)$ and $\alpha_m(JM)$ follow the cubic combinatorial rule also, therefore:

$$a_m(FM) = ((0.0494000)^{1/3} \times 0.7257 + (0.0178444)^{1/3} \times 0.2743)^3$$

$$= 0.0385993$$

$$c_m(GM) = ((2,545.0)^{1/3} \times 0.7257 + (475.00)^{1/3} \times 0.2743)^3$$

$$= 1,748.9$$

$$\delta_m(HM) = 0.08320 \times 10^6 \times (0.2743)^3$$

$$= 0.1717 \times 10^5$$

$$\alpha_m(JM) = ((0.000124359)^{1/3} \times 0.7257 + (0.00015300)^{1/3}$$

$$\times 0.2743)^3$$

$$= 0.000131824$$

The second and fourth virial coefficients may now be evaluated independent of the density.

$$C_1 = B_{om}RT - A_{om} - C_{om}/T^2 - D_{om}/T^4$$

$$= 0.0442135 \times 0.08206 \times 300.4 - 1.6648 - \frac{16,648.6}{(300.4)^2}$$

$$- \frac{5.73168 \times 10^5}{(300.4)^4}$$

$$= -0.753636$$

$$C_3 = a_m \alpha_m$$

$$= 0.385993 \times 0.000131824$$

$$= 0.508830 \times 10^{-5}$$

The third virial coefficient

$$C_2 = bRT - a + (C/T^2 - \delta/T^4)(1 + \gamma\rho^2)/e^{\gamma\rho^2})$$

can only be evaluated after a density has been estimated, and if

$$\rho = 0.93058 \text{ gm. moles/liter}$$

then

$$C_2 = 0.00306385 \times 0.8206 \times 300.4 - 0.0385993$$

$$+ \left(\frac{1,748.9}{(300.4)^2} + \frac{1.717 \times 10^4}{(300.4)^4}\right) \times \left(\frac{1 + (0.93058)^2 \times 0.006135}{\rho(0.93058)^2 \times 0.006135}\right)$$

$$= 0.0553097$$

The Pressure (PI) may now be evaluated from the equation of state

$$PI = RT + C_1\rho^2 + C_2\rho^3 + C_3\rho^6$$

$$= 0.08206 \times 300.4 - 0.75363 \times (0.930585)^2 + 0.0563097$$

$$\times (0.930585)^3 + 5.0883 \times 10^4 \times (0.930585)^6$$

$$= 22.332 \text{ atm.}$$

Since

$$PI = P$$

the density

$$\rho = 0.930585 \text{ gm. moles/liter}$$

is the correct density.

B. Calculation of Amount Loaded

1. Initial Amount in Feed Reservoir

Methane: $GMCI = V_{res} \times \rho_{INT} \times y_{CH_4} = VI \times DAI \times MFCHI$

$$= 961.1 \text{cc.} \times 0.000930585 \text{ gm.moles/liter} \times 0.7527$$

$$= 0.64906 \text{ gm.moles.}$$

Nitrogen: GMNI = 961.1 x 0.000930585 x 0.2473

= 0.24533 gm.moles.

2. Final Amount in Feed Reservoir

Density: DAF = 0.43538 gm.moles/liter at 155.7 psia and 300.4°K

Methane: GMCF = 972.2 x 0.00043538 x 0.7527

= 0.30718

Nitrogen: GMNF = 972.2 x 0.00043538 x 0.2473

= 0.11611

3. Net Amount Loaded Into Cell

Methane: LOADC = GMCI - GMCF

= 0.64906 - 0.30718

= 0.34188 gm.moles

Nitrogen: LOADN = 0.12922

C. Calculation of Equilibrium Amount Adsorbed

1. Experimental Data

Pressure: PC = 111.7 psia

Temperature: TC = 174.87°K

Free Space: VC = 89.72 cc.

Gas Phase Comp, CH_4, MFCH = 0.4908

N_2, MFN = 0.5092

2. Computation

Pressure: PC = 111.7/14.696 = 7.60 atm.

Density: DAC = 0.0005558 gm.moles/liter

Amount in Gas Phase

Methane: GMGC = VC x DAC x MFCH

= 89.72 x 0.0005558 x 0.4908

= 0.024476

GMGN = 89.72 x 0.0005558 x 0.5092

= 0.02539

Amount in Adsorbed Phase

GAC = LOADC - GMGC

= 0.34188 - 0.02448

= 0.3174

GAN = 0.12922 - 0.025394

= 0.103828

XC = GAC/GAN + GAC

XC = 0.7535

Relative Volatity

α = (MFN/XN)/(MFCH/XC)

= 3.28

D. Desorption or Amount Lost in Sampling

Sample calculation for first desorption

1. Experimental Data

Pressure: PS = 12.447 psia

Volume: VS = 11,780 cc.

Temperature: TS = 301.5

Composition: MFCH = 0.6949, MFN = 0.3051

2. Calculation

DAS = 0.000034 gm. moles/cc.

Desorbed DELC = VS x DAS x MFCH

= 11,780 x 3.4 x 10^{-5} x 0.6949

= 0.2805 gm. moles

DELN = 11,780 x 3.4 x 10^{-6} x 0.3051

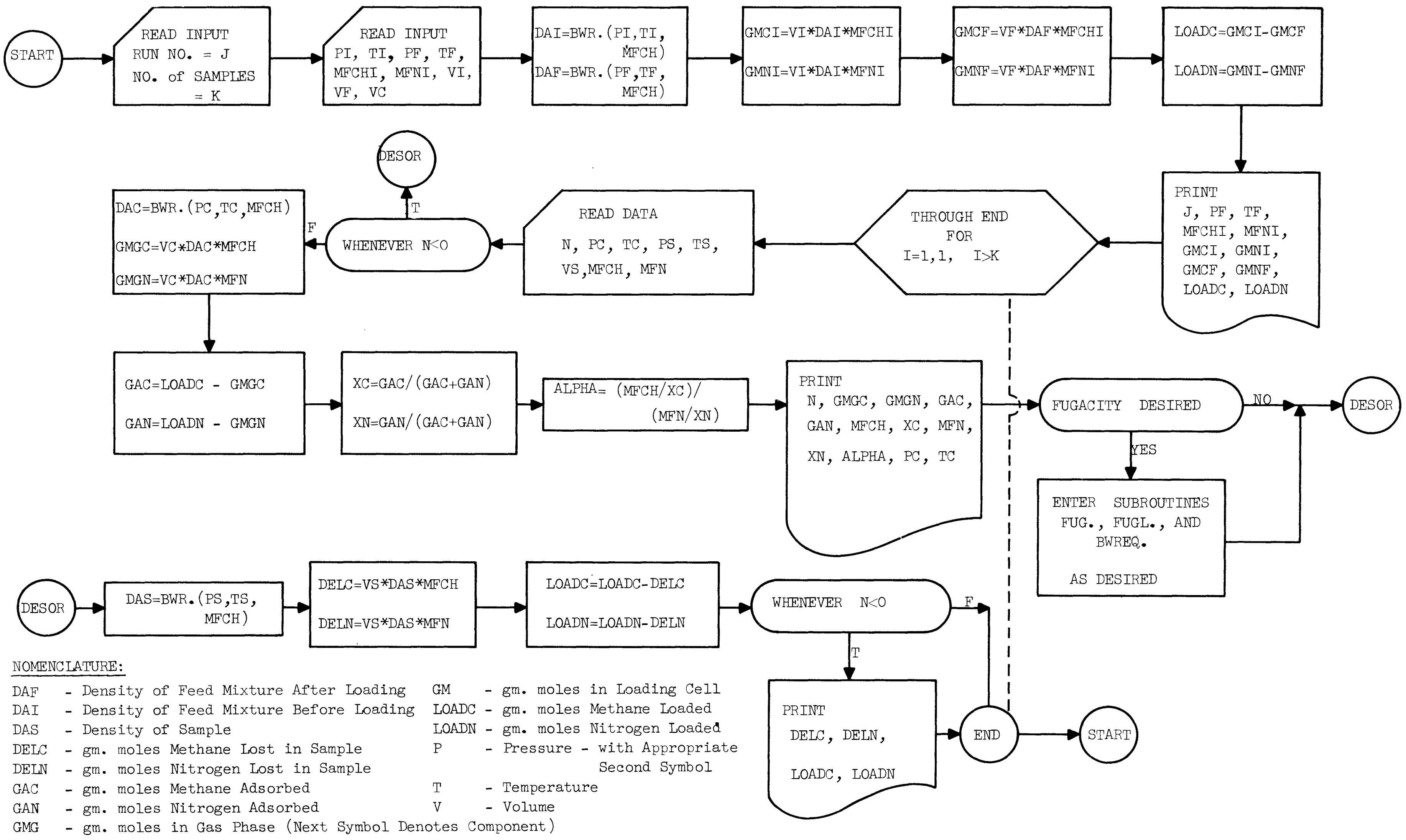
= 0.1231 gm. moles

Net Remaining in System

Methane $LOADC_{i-1}$ = $LOADC_i$ - DELC

= 0.34188 - 0.2805

= 0.0613 gm. moles



NOMENCLATURE:

DAF - Density of Feed Mixture After Loading
DAI - Density of Feed Mixture Before Loading
DAS - Density of Sample
DELC - gm. moles Methane Lost in Sample
DELN - gm. moles Nitrogen Lost in Sample
GAC - gm. moles Methane Adsorbed
GAN - gm. moles Nitrogen Adsorbed
GMG - gm. moles in Gas Phase (Next Symbol Denotes Component)
GM - gm. moles in Loading Cell
LOADC - gm. moles Methane Loaded
LOADN - gm. moles Nitrogen Loaded
P - Pressure - with Appropriate Second Symbol
T - Temperature
V - Volume

Figure 30. Computer Flow Diagram for Equilibrium Adsorption Loading Calculation.

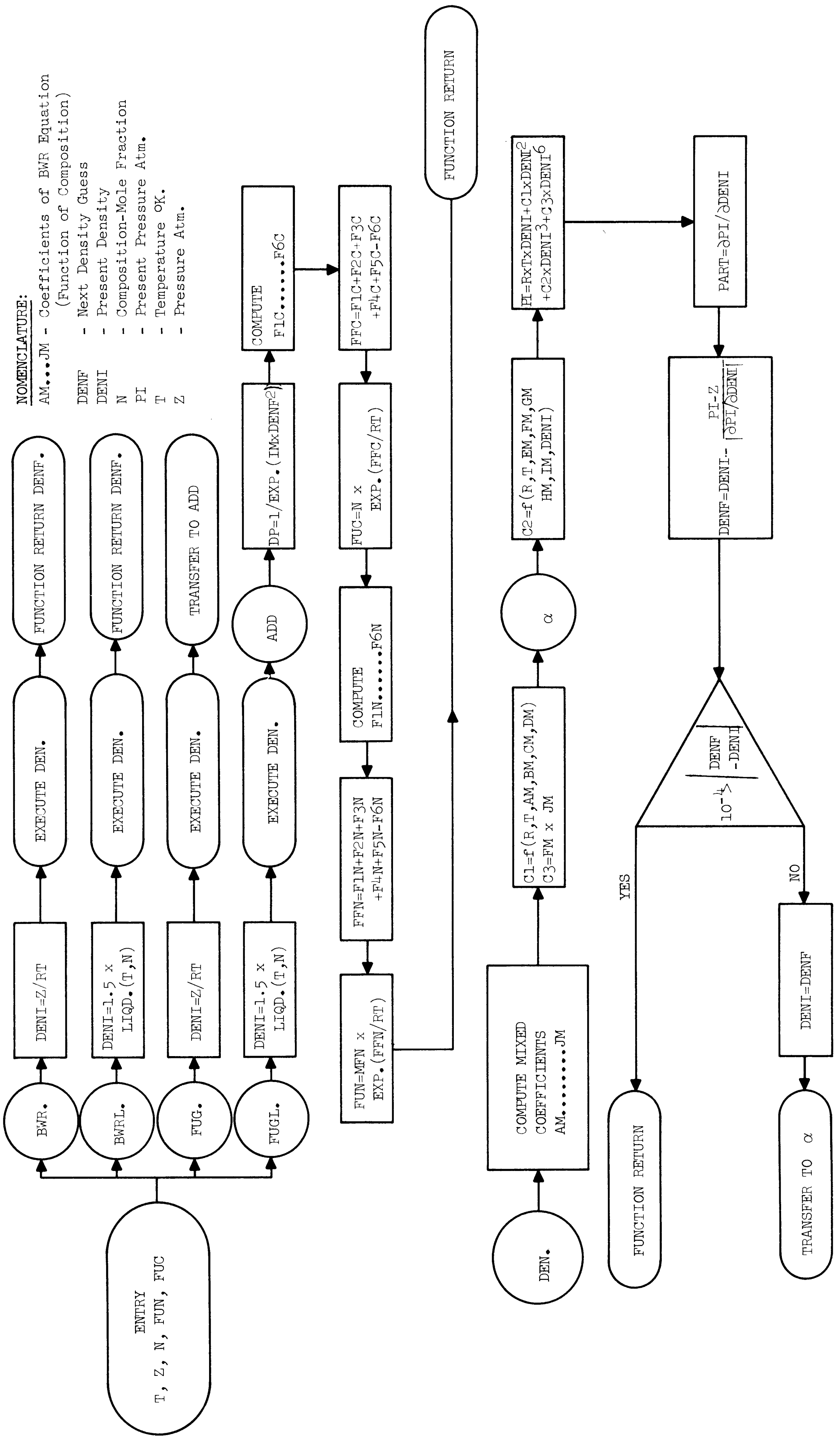


Figure 31. Computer Flow Diagram for B-W-R Equation Solution for Density and Fugacity

TABLE XXVII

SAMPLE PRINT OUT FROM COMPUTER CALCULATION

```
ADSORPTIVE EQUILIBRIUM CH4-N2
RUN NO.  76
INITIAL CONDITIONS
    INT.PRESS= 10.59  ATM.    INT. TEMP = 300.4  KELVIN
   M.FRAC.CH4=0.7257    M.FRAC.N2 =0.2743
  G.MOL1CH4= 0.64906    G.MOL1.N2  = 0.24533    G.MOL2.CH4= 0.30718    G.MOL2.N2  = 0.11611
   LOADED   G.MOL.CH4= 0.34188   G.MOL.N2 = 0.12922

SAMP      G.MOLES CH4            G.MOLES N2             MOLE FRAC. CH4        MOLE FRAC. N2   ALPHA
 NO    GAS          ADSORB         GAS          ADSORB       GAS        ADSORB   GAS     ADSORB
 1    0.024476     0.317400     0.025294     0.103926     0.49080     0.75351    0.50920 0.24649    0.315  7.60 174.9
          1 FUGACITY-GAS PHASE  CH4 =     3.47222      N2=     3.77847      TOTAL=     7.25561
        VAP. DENSITY=     0.55584    GMM/L
SAT.VALUES
    CH4-TEMP=  143.06409   DENSITY=    23.81894   GMM/L
     N2-TEMP=    99.87026   DENSITY=  24.84852   GMM/L
    MIXTURE DENSITY=   24.06463   GMM/L
    SAT.VAP.PRESS.  CH4=    28.14911   N2=  156.57950   MIXTURE=   93.54537   ATM
    SAT. DENSITY=   14.76709GMM/L
    FS(CH4)=  14.35203   FS(N2)=  38.61521   FS(MIX)=   48.73835
    N*V(T)=   0.19769737   N*V(CH4)=   0.15065651   N*V(N2)=   0.04724085   CC/GRAM
    LN(FS/F)/V=   0.04583569   GMMOL/CC      T*LN(FS/F)/V=   8.01528692   K GMMOL/CC
    LN(SUMFS/SUMF)/V=   0.04785440
-2                 GMOL.CH4 DESORBED=      0.280508      GMOL. N2 DESORBED=      0.123158
                 GMOL.   IN CELL-CH4=     0.060857      N2=      0.005533

-3                 GMOL.CH4 DESORBED=      0.058182      GMOL. N2 DESORBED=      0.000000
                 GMOL.   IN CELL-CH4=     0.002675      N2=      0.005533

-4                 GMOL.CH4 DESORBED=      0.004074      GMOL. N2 DESORBED=      0.000000
                 GMOL.   IN CELL-CH4=   -0.001399      N2=      0.005533
```

APPENDIX F

ADSORPTION OF HELIUM

During the early exploratory work, a number of runs was made to determine the adsorption of helium at higher pressures. Several runs were made at room temperature as well as one at -68°C and one at -197°C. The results are listed in Table XXVII below.

TABLE XXVIII

ADSORPTION OF HELIUM

Temp. °C	Pressure ATM	Amount Adsorbed milligram moles/gm.
21	71.45	0.0
21	41.17	0.0
-68	44.2	2.0
-197	27.2	2.9

The experimental procedure was identical to that used in determining methane and nitrogen equilibrium.

The calculation of the equilibrium amount adsorbed was similar to that outlined in Appendix E which shows a sample calculation for methane-nitrogen adsorption. The P-V-T behavior of helium at room temperature was represented by the Beattie-Bridgman equation with appropriate constants. At the lower temperatures, -68°C and -197°C, the reduced state correlation of Hamrin and Thodos(23) was used to obtain the gas phase density of helium.

One determination of the adsorption equilibria of a mixture of nitrogen and helium was made at room temperature. The data from this run, though inconclusive, indicate that the helium acts as a diluent at this temperature. The amount adsorbed was, however, about fifteen per cent greater that would be expected if one assumes an ideal mixture between the two components.

The results obtained in this exploratory study are included to serve as a guide for future work as the helium-nitrogen system is of particular interest today from a conservation standpoint.

BIBLIOGRAPHY

1. Antropff, von A. Kolloid Z., 129, 11 (1952).

2. "Boiler and Pressure Vessel Code." ASME, Sect. VIII, 1956ed., 7-12, 109-113.

3. Baly, E. C. C. Proc. Roy. Soc., A160, 465 (1937).

4. Barrer, R. M. J. Soc. Chem. Ind., 64, 130 (1945).

5. Bartlett, E. P. J. Am. Chem. Soc., 49, 687 (1927).

6. Benedict, M., Webb, G. B. and Rubin, L. C. J. Chem. Phys., 8, 334 (1940).

7. Ibid, 10, 747 (1942).

8. Berényi, L. L. Z. Physik. Chem., 94, 628 (1920).

9. Berényi, L. L. Z. Angw. Chem., 35, 237 (1922).

10. Bloomer, O. T., Parent, J. D. I.G.T. Bull. No. 17, 1952.

11. Bloomer, O. T., Roa, K. N. I.G.T. Bull. No. 18, 1952.

12. Breck, D. W., Eversole, W. G., Milton, R. M., Reed, T. B., and Thomas, T. L. J. Am. Chem. Soc., 78, 5963 (1956).

13. Brunauer, S. The Adsorption of Gases and Vapors, Vol. I, Princeton Univ., Princeton, 1945.

14. Brunauer, S., Demming, L. S., Demming, W. E. and Teller, E. J. Am. Chem. Soc., 62, 1723-32 (1940).

15. Brunauer, S., Emmet, P. and Teller, E. J. Am. Chem. Soc. 60, 309 (1938).

16. Coolidge, A. S. J. Am. Chem. Soc., 46, 596 (1924).

17. Darby, H. S. Pressure - Volume - Temperature Relationship of Methane - Nitrogen Mixtures at Low Temperatures, Unpublished Master's Thesis, I.G.T., 1951.

18. Dubinin, M. M. Chem. Rev., 60, 235 (1960).

19. Ellington, R. T., Bloomer, O. T., Eakin, B. E. and Gami, D. C. "Thermodynamic and Transport Properties of Gases, Liquids and Solids," ASME, New York, 102 (1959).

20. Fowler, R. H. and Guggenheim, E. A. Statistical Thermodynamics, Macmillan, New York, 1939.

21. Freundlich, H. Colloid and Capillary Chemistry, Methuen and Co., London, 1926.

22. Goldman, F. and Polanyi, M. Z. Physik. Chem., A132, 321 (1928).

23. Hamrin, C. E. Jr. and Thodos, G. AIChE Journal, 4, 480 (1958).

24. Hill, T. L. J. Chem. Phys., 14, 263 (1946).

25. Ibid., 268-7.

26. Hill, T. J. Am. Chem. Soc., 72, 5347 (1950).

27. Hiza, M. J. Chem. Eng. Progr., 56, No. 10, 68 (1960).

28. Honig, J. M. Anal. N. Y. Acad. Sci., 58, 741 (1958).

29. Johnson, V. J. Adv. in Cryogenic Eng., 3, Paper A-2, Plenum Press, New York, 1960.

30. Josefowitz, S. and Othmer, D. F. Ind. Eng. Chem., 40, 739 (1948).

31. Joyner, L. G., Weinberger, E. B. and Montgomery, C. W. J. Am. Chem. Soc., 67, 2182 (1945).

32. Keyes, F. G. and Burks, H. G. J. Am. Chem. Soc., 50, 1100 (1928).

33. Langmuir, I. Phys. Rev., 8, 149 (1916).

34. Langmuir, I. J. Am. Chem. Soc. 40, 1361 (1918).

35. Lee, V. J. Unpublished Paper, University of Michigan, 1959.

36. Lewis, W. K., Gilliland, E. R., Chertow, B. and Codogan, W. P. Ind. Eng. Chem., 42, 1319 (1950).

37. Ibid., 1326 (1950).

38. McBain, J. W. and Bakr, A. M. Jr. J. Am. Chem. Soc., 48, 690 (1926).

39. McBain, J. W. and Britton, G. T. J. Am. Chem. Soc., 52, 2198 (1930).

40. Markham, E. D. and Benton, A. F. J. Am. Chem. Soc., 53, 497 (1931).

41. Milne, W. E. Numerical Calculus, Princeton University, Princeton, 1949.

42. Morris, H. E. and Mass, O. Can. J. Res., 9, 240 (1923).

43. Nikolaev, K. M. and Dubinin, M. M. Izvest. Akad. Nauk SSSR, Otdel. Kheim. Nauk, 1165 (1958).

44. Pace, J. C. Compressibility Factors of Nitrogen, Methane, and Three of Their Mixtures. Unpublished Master's Thesis, I. G. T., 1951.

45. Pease, R. N. J. Am. Chem. Soc., 45, 1196 (1923).

46. Peierls, R. Proc. Camb. Phil. Soc., 32, 471 (1936).

47. Polanyi, M. Ber. Deut. Physik. Ges., 16, 1012 (1914).

48. Polanyi, M. Ver. Deut. Physik. Ges., 18, 55 (1916).

49. Polanyi, M. Z. Electrochemie, 26, 370 (1920).

50. Polanyi, M. Z. Physik. Chem., A138, 459 (1928).

51. Rabe, A. and Thomas, T. L. Private Communication.

52. Redlich, O. and Peterson, D. L. J. Phys. Chem., 63, 1024 (1959).

53. Reed, T. B. and Breck, D. W. J. Am. Chem. Soc., 78, 5972 (1956).

54. Rideal, E. K. Surface Chemistry, Cambridge University, Cambridge, 1930.

55. Sault, R. A. Compressibility of Certain Methane - Nitrogen Mixtures. Unpublished Master's Thesis, I.G.T., 1952.

56. Schay, G. J. Chem. Phys., (Hungary), 53, 691 (1956).

57. Schay, G. Fejes, P. and Szethmary, J., Acta Chim. Aca. Sci., Hungary, 12, 299 (1957).

58. Sips, R. J. Chem. Phys., 16, 490 (1948).

59. Ibid., 18, 1024 (1950).

60. Tarpnell, B. M. W. Chemisorption. Butterworth, London, 1955.

61. Wang, J. Proc. Roy. Soc., A161, 127 (1938).

62. Williams, A. M. Proc. Roy. Soc., Edinburg, 38, 23 (1917-18).

63. Zeldowitsch, J. Acta Physiochim. USSR, 1, 961 (1934).